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ON THE MEAN CONSERVING PROPERTY

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1. Introduction

It is the object of this paper to investigate into the general forms of the distribution laws which possess the mean conserving property and arrive at new frequency curves useful for graduation purposes and in tests of significance connected with means in random samples.

The mean conserving property may be defined as follows. Let a variate x be characterised by the probability differential

$$df = \phi(x, \lambda, \mu, \ldots) dx \qquad (1\cdot1)$$

$\lambda, \mu, \ldots$ being constants which may be called the parameters in the distribution law of x. Let $x_1, x_2, \ldots$ be independent variates from distribution laws of the type (1·1) defined by the sets of parameters given as rows of the matrix

$$\begin{pmatrix} \lambda_1 & \mu_1 & \ldots \\ \lambda_2 & \mu_2 & \ldots \\ \ldots & \ldots & \ldots \end{pmatrix} \qquad (1\cdot2)$$

The type (1·1) is said to possess the mean conserving property denoted by

$$M^{\alpha, \beta, \nu, \ldots}_{\xi, \eta, \zeta, \ldots} \qquad (1\cdot53)$$

where $\alpha, \beta, \gamma, \ldots$ and $\xi, \eta, \zeta, \ldots$ are the sets of parameters which have to be kept fixed and can be varied in the distribution laws of $x_1, x_2, \ldots$ if their mean follows the distribution law of the same type as in (1·1) but with the set of parameters

$$(\lambda, \mu, \ldots), \qquad (1\cdot4)$$

where $\lambda, \mu, \ldots$ are functions of the number of x's and the elements of the matrix (1·2).

A similar definition holds for the sum conserving property defined by

$$S^{\alpha, \beta, \gamma, \ldots}_{\xi, \eta, \zeta, \ldots} \qquad (1\cdot5)$$

Both (1·3) and (1·5) can be made identical by the introduction of a new constant as a multiplier of x, and the property (1·3) or (1·5) will be referred to as M.

2. Properties of Distribution Laws Satisfying M

From the definition of M we derive the relations

$$\prod_{r=1}^{n} c\,(t,\ \lambda_r,\ \mu_r, \ldots.) = c\,(t,\ \lambda,\ \mu, \ldots..) \tag{2·1}$$

$$\sum_{r=1}^{n} k_s\,(\lambda_r,\ \mu_r, \ldots..) = k_s\,(\lambda,\ \mu, \ldots.) \tag{2·2}$$

where $c\,(t)$ is the characteristic function corresponding to the distribution law of x and k_s, the sth semi-invariant of x.

These simple properties enable us to discover readily whether any distribution law satisfies M when a study of its moments and semi-invariants are made. Let us consider the Bessel function populations defined by

$$\mathrm{T}_0\, e^{-\frac{c}{b}x}\ |x|^m \begin{Bmatrix} \Pi\ \mathrm{I}_m\,(x) \\ k_m\,(x) \end{Bmatrix} dx \tag{2·3}$$

where the upper function is taken when $|c| > 1$ and the lower when $|c| < 1$. The moment generating function, in either case, is given by

$$\{f\,(t,\ b,\ c)\}^{m+\frac{1}{2}} = \{(1-c^2)/(1-c+tb)\}^{m+\frac{1}{2}} \tag{2·4}$$

Since

$$\prod_{r=1}^{n} \{f\,(t,\ b,\ c)\}^{m_r+\frac{1}{2}} = \{f\,(t,\ b,\ c)\}^{mn+\frac{n}{2}} \tag{2·4}$$

where

$$mn = m_1 + m_2 + \cdots + m_n \tag{2·5}$$

it follows that the sum of n variates from populations of the type (2·3) defined by

$$\begin{pmatrix} b & c & m_1 \\ b & c & m_2 \\ .. & .. & .. \\ b & c & m_n \end{pmatrix} \tag{2·6}$$

follows the same type defined by

$$(b \quad c \quad n(m+\tfrac{1}{2}) - \tfrac{1}{2}) \tag{2·7}$$

For the Bessel function population defined by

$$\mathrm{T}_0 = x^{\frac{m}{2}}\ e^{-ds}\ \mathrm{I}_m\,(q\sqrt{x})\ dx \tag{2·8}$$

the sth semi-invariant is given by

$$k_s = (s-1)\,!\,\left\{\frac{(m+1)}{\alpha^s}+\frac{q^2}{4}\,\frac{s}{\alpha^{s+1}}\right\}. \tag{2·10}$$

Hence the sth semi-invariant of $nz = x_1 + x_2 + \ldots\ldots + x_n$ where x_i follows the law (2·8) with the parameters α, m_i, q_i is given by

$$k_s = (s-1)\,!\,\left\{\frac{n\,(n+1)}{\alpha^s}+\frac{nq^2}{4}\,\frac{s}{\alpha^{s+1}}\right\} \tag{2·10}$$

where $$mn = m_1 + m_2 + \ldots. + m_n$$

and $$nq^2 = q_1^2 + q_2^2 + \ldots. + q_n^2$$

which shows that (2·8) satisfies $\mathrm{M}^{\mathrm{c}}{}_{m,q}$, the set of parameters

$$\begin{pmatrix} \alpha & m_1 & q_1 \\ .. & .. & .. \\ \alpha & m_n & q_n \end{pmatrix} \tag{2·11}$$

giving the set

$$(\alpha \quad n\,(m+1)-1 \quad \sqrt{n}q) \tag{2·12}$$

for the distribution of the sum. This result has been obtained by Bose (1937) when m's and q's are the same for all the variables.

If $k_s(r)$, $r = 1, 2, \ldots. n$ are the semi-invariants of the variates $x_1, x_2, \ldots. x_n$, the distribution laws of which satisfy M, then the semi-invariants of the variate $\mathbf{Z} = x_1 + x_2 + \ldots. + x_n$ satisfy (2·2). Hence we get the result that *the distribution law of the sum or the mean of any number of independent variates, whose distribution laws satisfy M, also satisfies M.* From this it follows that the distribution law

$$df = c\,e^{-\alpha_i x}\,x^{n\lambda-1}\sum_{m=0}^{\infty}\frac{m!\,\mathrm{A}_m\,\mathrm{Z}^m}{\Gamma(n\lambda+m)} \tag{2·13}$$

$$n\lambda = \lambda_1 + \lambda_2 + \cdots + \lambda_n$$

$$\mathrm{A}_m = \frac{d^m}{da^m}\left[\prod_{j=1}^{n}\{1-(\alpha_i-\alpha_j)\,a\}^{-\lambda_j}\right]_{a=0}$$

derived by the author (1942) as the distribution of the sum of n different gamma variates following the laws

$$c\,e^{-\alpha_r x}\,x^{\lambda_r-1}\,dx \tag{2·14}$$

$$r = 1, 2, \ldots., n$$

satisfies M.

It is well known that the distribution law

$$\frac{\alpha^\lambda}{\Gamma(\lambda)}\,e^{-\alpha x}\,x^{\lambda-1}\,dx \tag{2·15}$$

satisfies M^{α}_{λ}. Let the variates $x_1, x_2, \ldots, x_n$ have the probability densities

$$f(x_r, a_r, b_r, \ldots) \qquad (2\cdot16)$$

$$r = 1, 2, \ldots n$$

with the corresponding cumulant functions

$$S(\beta, a_r, b_r, \ldots) \qquad (2\cdot17)$$

If it is known that the distribution of $Z = x_1 + x_2 + \ldots + x$ is (2·15) with the cumulant function $-\lambda \log (1 - i\beta/\alpha)$ then by hypothesis we have

$$\sum_{r=1}^{n} S(\beta, a_r, b_r, \ldots) = -\lambda \log (1 - i\beta/\alpha) \qquad (2\cdot18)$$

or

$$\sum_{r=1}^{n} F(\beta, a_r, b_r, \ldots) = -\lambda \qquad (2\cdot19)$$

where $F(\beta) = S(\beta)/\log (1 - i\beta/\alpha)$. Differentiating (2·19) with respect to β we get

$$\Sigma F'(\beta,) a_r, b_r, \ldots) = 0 \qquad (2\cdot20)$$

If this holds for all sets of $a_r, b_r, \ldots$ then we get by setting them equal values for all r, that

$$n F'(\beta, a, b, \ldots) = 0 \qquad (2\cdot21)$$

or

$$S(\beta, a, b, \ldots) = c \log (1 - i\beta/\alpha) \qquad (2\cdot22)$$

where c must necessarily be negative if the right-hand side is to represent a cumulant function. Hence $f_r(x_r, a_r, b_r, \ldots)$ is of the gamma type. So we get the result that *if the sum of* n *independent variates drawn from* n *different populations of the same type (the mathematical form remaining the same and the parameters may be varying) follows the gnmma type distribution law, then the above original populations also belong to the gamma type.* As a result of this we get the necessary and sufficient condition for the sum of n into pendent observations from a population to follow the gamma type is that the population itself is of the gamma type. Also it easily follows that *if the sum of two variates of which one follows the gamma type, is distributed in the gamma type, then the other variate also follows the gamma type.*

3. Differential Equation Satisfied by the Characteristic Function

When all the n variates are drawn from the same population, we have, if $c(t)$ represents the characteristic function of the distribution in the population satisfying M,

$$\{c(t, \lambda', \mu', \ldots)\}^n = c(t, \lambda, \mu, \ldots). \qquad (3\cdot1)$$

Taking logarithms and representing $\log c(t)$ by $\psi(t)$ we get

$$n\psi(t, \lambda', \mu', \ldots) = \psi(t, \lambda, \mu, \ldots). \tag{3·2}$$

Starting from $\psi(t, \lambda', \mu', \ldots)$ we can form the differential equation satisfied by ψ under some analytical conditions by eliminating the constants $\lambda', \mu', \ldots$. The order of the differential equation is, in general, equal to the number of constants eliminated. Since $\psi(t, \lambda, \mu, \ldots)$ also should satisfy this equation, we require that ψ and $n\psi$ should both satisfy the differential equation for ψ. If the differential equation satisfied by ψ is

$$D(\psi, \psi' \ldots) = 0 \tag{3·3}$$

then

$$D(n\psi, n\psi', \ldots) = 0 \tag{3·4}$$

which shows that D must be homogeneous in $\psi, \psi', \psi'', \ldots$ the homogeneity of $D(x, y, \ldots)$ being defined as

$$D(ax, ay, \ldots) = f(a)\, D(x, y, \ldots) \tag{3·5}$$

The differential equation (3·4) may be denoted by $D_H = 0$. Hence we get the results that *the semi-invariant generating function corresponding to a distribution law satisfying M satisfies a homogeneous differential equation homogeneity being defined as in* (3·5).

From the above differential equation $D_H = 0$, we can derive the differential equation satisfied by $c(t)$ by making the substitutions

$$\psi = \log c, \quad \psi' = c'/c \text{ etc.} \tag{3·6}$$

If the differential equation $D_H = 0$ arising out of the probability differential $\phi(x)\,dx$ is homogeneous then the differential equation arising out of the probability differential $\chi(a)\, e^{ax}\, \phi(x)\, dx$ is also homogeneous which shows that the property M is conserved by the multiplication of the distributive law by an exponential factor.

We shall now consider some distribution laws obtained by inversion from $D_H = 0$. The simplest case is when the order of $D_H = 0$ is one, in which case the differential equation becomes

$$\frac{\psi'}{\psi} = f(t) \text{ (an arbitray function)} \tag{3·7}$$

which gives the solution

$$\psi = \lambda\, e^{\phi(t)} \text{ where } \phi(t) = \int f(t)\, dt \tag{3·8}$$

and $c(t) = e^{\psi}$. If $e^{\phi(t)}$ admits an expansion in series we get

$$c(t) = e^{\lambda\left(a_0 + a_1 \frac{it}{1!} + a_2 \frac{(it)^2}{2!} + \cdots\right)}$$

which shows the $\lambda a_1, \lambda a_2, \ldots$ are the semi-variants of the distribution. In particular if $a_1, a_2, \ldots$ are the semi-invariants for any distribution law then $na_1, na_2, \ldots$ are the semi-invariants for the sum of n independent observations from the above distribution. This gives the result that *the distribution law of the sum or mean of a number of observations from any distribution law with finite semi-invariants satisfies M.* The functional form of the distribution law may change with n but may be capable of being represented by a general type of function. Thus we get a huge class of distribution laws satisfying M.

4. Measures of Departure from M

Given the probability density $\phi_1(x, \lambda, \mu, \ldots)$ of a variate x, we can, in general, replace the constants $\lambda, \mu, \ldots$ by an equivalent number of semi-invariants of suitable orders so that $\phi_1(x, \lambda, \mu, \ldots)$ may be written as $\phi(x, k_1, k_2, \ldots)$ where $k_1, k_2, \ldots$ are the first, second, etc., semi-invariants. Let the cumulant generating function be $k(t, k_1, k_2, \ldots)$. Then the cumulant generating function of the mean of n observations is $nk(t, k_1, k_2, \ldots)$. Let $R(t, n, k_1, k_2, \ldots)$ be defined by

$$n k\left(\frac{t}{n}, k_1, k_2 \ldots\right) = k(t, k_1, k_2/n, \ldots) + R(t, n, k_1, \ldots). \tag{4·1}$$

When the distribution law satisfies M, R vanishes. If not, it can be written, when it admits expansion, as

$$R(t, n, k_1, \ldots) = \sum_{\rho=s}^{\infty} \frac{a_\rho}{\rho!} t^\rho \tag{4·2}$$

where s depends on the number of constants involved in the distribution law of x. Taking the exponentials in (4·1) we get

$$e^{nk\left(\frac{t}{n}, k_1, k_2, \cdots\right)} = e^{k(t, k_1, k_2/n, \cdots)}\left(1 + \sum_{\rho=s}^{\infty} \frac{b_\rho}{\rho!} t^\rho\right). \tag{4·3}$$

On taking the integral transform we get the probability density $S(z)$ of the mean as

$$S(z) = \phi(z, k_1, k_2/n, \cdots) + \sum_{\rho=s}^{\infty} \frac{b_\rho}{\rho!} \frac{d^\rho}{dz^\rho} \phi(z). \tag{4·4}$$

The expression consists of two portions. The second part vanishes when M holds and measures the departure from M when M does not hold. The considerations of replacing $S(z)$ by $\phi(z, k_1, k_2/n, \ldots)$ depend upon the magnitude of this measure. It is proposed to study the effect of the departure from M when n increases and also to consider the effect of replacing $\phi(z, k_1, k_2/n)$ by the normal approximation.

5. Series in Orthogonal Polynomials

Let $M(\alpha)$ be the *m.g.f.* of a variate whose distribution law satisfies M and $f(\alpha)$ any arbitrary function. If

$$G_1 = M_1(\alpha) \sum_{\gamma=0}^{\infty} \frac{a_r}{r!} \{f(\alpha)\}^r \tag{5·1}$$

$$G_2 = M_2(\alpha) \sum_{\gamma=0}^{\infty} \frac{b_r}{r!} \{f(\alpha)\}^r \tag{5·2}$$

are the *m.g.f.*'s of x_1 and x_2 following the distribution laws

$$\phi(x, \lambda_1, \mu_1, \ldots.)\, dx \tag{5·3}$$

$$\phi(x, \lambda_2, \mu_2, \ldots.)\, dx \tag{5·4}$$

then the *m.g.f.* of $z = x_1 + x_2$ is

$$G = G_1 G_2 = M_1 M_2 \sum_{l=0}^{\infty} \sum_{l=r+s} \frac{a_r}{r!} \frac{b_s}{s!} f^l \tag{5·5}$$

$$= M_3 \sum_{l=0}^{\infty} \frac{c_l}{l!} f^l.$$

The functional form of G will be same as that of G_1 and G_2 if the same holds for c_l and a_r and b_r *i.e.*, a_r satisfies the recurrence relation

$$\sum_{r+s=l} \frac{a_r}{r!} \frac{b_s}{s!} = \frac{c_l}{l!} \tag{5·6}$$

where b_s and c_l are of the same form as a_r differing only in the parameters involved in them. If (5·6) holds then by successive applications we can show that

$$G = G_1 G_2 \ldots . G_n \tag{5·7}$$

has the same functional form as G_i. By a suitable selection of $M(\alpha)$ and $f(\alpha)$ we can get several distribution laws satisfying M.

Let $M(\alpha) = (1-\alpha)^{-p}$ and $f(\alpha) = \alpha/(1-\alpha)$

Since $(1-\alpha)^{-p}\, \alpha^r/(1-\alpha)^r$

$$= \frac{(-1)^r\, \alpha^r}{p\,(p+1) \cdots (p+r-1)} \frac{d^r}{d\alpha^r} (1-\alpha)^{-p}$$

i.e., the *m.g.f.* corresponding to

$$\frac{\Gamma(p)}{\Gamma(p+r)} L_r(x, p)\, \phi(x) \tag{5·8}$$

where $\phi(x) = e^{-x}\, x^{p-1}/\Gamma(p)$ and $L_r(x, p) = \left(\frac{-d}{dx}\right)^r x^r\, \phi(x)$ we see that $(1-\alpha)^{-p}\left(a_0 + \frac{a_1}{1!} f(l) + \cdots\right)$ is the *m.g.f.* of

$$\gamma(x) = \phi(x) \sum_{\gamma=0}^{\infty} \frac{a_r}{r!} \frac{\Gamma(p)}{\Gamma(p+r)} L_r(x, p) \tag{5·9}$$

where a_r satisfies (5·6). This is a series in Lagurre's polynomials satisfying M.

Let $M(a) = e^{a^2\sigma^2}$, $f(a) = a$. We get that

$$e^{a^2\sigma^2} \sum_{r=0}^{\infty} \frac{a_r}{r!} a^r \tag{5·10}$$

is the *m.g.f.* of

$$\psi(x) = \text{const.}\, e^{-\frac{x^2}{2\sigma^2}} \left(a_0 + \frac{a_1}{1!} H_1 + \frac{a_2}{2!} H_2 + \cdots \right), \tag{5·11}$$

where $$H_\rho = e^{\frac{x^2}{2\sigma^2}} \frac{d^\rho}{dx^\rho} e^{-\frac{x^2}{2\sigma^2}},$$

which is a series in Hermite polynomials satisfying M if a_r satisfies (5·6). By suitable selections of $M(a)$ and $f(a)$ we can obtain the development of probability functions satisfying M in a series of Bessel functions (Neumann's expansion) involving $J_n(x)$, Hypergeometric and other suitable functions. These are omitted here as they are not of direct interest in graduation or tests of significance.

6. Some Special Series

A series of the form

$$c\, e^{-ax} x^m \sum \frac{a_r}{r!} x^r \tag{6·1}$$

is of special interest for the gamma type distribution occurs as a generating function. We shall investigate into the nature of a_r so that (6·1) satisfies M. If x and y follow the type (6·1) with the parameters

$$\begin{pmatrix} a & \lambda & m_1 & p_1 & \cdots \\ a & \lambda & m_2 & p_2 & \cdots \end{pmatrix} \tag{6·2}$$

then the distribution of $z = x + y$ is given by

$$c'\, e^{-az}\, dz \frac{d}{dz} \iint_{\Omega} \sum \sum \frac{a_r}{r!} \frac{b_s}{s!} x^{m_1+\lambda r} y^{m_2+\lambda s}\, dx\, dy \tag{6·3}$$

where the integral is over the domain Ω defined by $x > 0$, $y > 0$ and $x + y < z$. This becomes apart from const. $e^{-az}\, dz$,

$$\begin{aligned} &\frac{d}{dz} \sum \sum \frac{a_r}{r!\, \Gamma(m_1 + \lambda r + 1)} \frac{b_s}{s!\, \Gamma(m_2 + \lambda s + 1)} \\ &\qquad \times \frac{z^{m_1 + m_2 + \lambda(r+s) + 2}}{\Gamma(m_1 + m_2 + \lambda(r+s) + 3)} \\ &= \sum \sum \frac{a_r' b_s'}{r!\, s!} \frac{z^{m_1 + m_2 + \lambda(r+s) + 1}}{\Gamma(m_1 + m_2 + \lambda(r+s) + 2)} \end{aligned} \tag{6·4}$$

where

$$a_r' = a_r/\Gamma(m_1 + \lambda r + 1)$$

$$b_s' = b_s/\Gamma(m_2 + \lambda s + 1)$$

The distribution of Z now becomes

$$c'' e^{-az}\, dz \sum_{l=0}^{\infty} \frac{A_l'}{l!} \frac{z^{m_1 + m_2 + \lambda l + 1}}{\Gamma(m_1 + m_2 + \lambda l + 1)}$$

$$= c = e^{-az}\, dz \sum_{l=0}^{\infty} \frac{A_l}{l!} z^{m + \lambda l}$$

where $m = m_1 + m_2 + 1$ and

$$A_l\, \Gamma(m_1 + m_2 + \lambda l + 1) = A_l' = l! \sum\sum_{r+s=l} \frac{a_r'}{r!} \frac{b_s'}{s!}$$

which shows that (6·1) satisfies M if a'_r satisfies (5·6). The method of proof can be extended to the sum of n variates. Some particular forms of a'_r give rise to important distribution laws.

(*a*) $a'_r = q^r$ then (6·1) satisfies $M^{\alpha, \lambda}_{m, q}$

(*b*) $a'_r = \Gamma\left(\frac{m+1}{\lambda} + r\right)$ satisfies $M^{\alpha, \lambda, q}_{m}$

(*c*) $a'_r = \Gamma(p + r)\, q^r$ satisfies $M^{\alpha, \lambda, q}_{p, m}$

(*d*) $a'_r = \sum_{\gamma_1 + \gamma_2 + \ldots = r} \Gamma(p_1 + r_1)\, q_1^{r_1}\, \Gamma(p_2 + r_2)\, q^{r_2}$ satisfies $M^{\alpha, \lambda, q_1, q_2, \ldots}_{m, p_1, p_2, \ldots}$

The solutions for (*a*), (*b*), (*c*) and (*d*), in the special case $\lambda = 1$, become

(*a*) $c\, e^{-dx}\, x^{\frac{m}{2}}\, I_m(q\sqrt{x})$

(*b*) $c\, e^{-ax}\, x^m\, I_m(qx)$

(*c*) $c\, e^{-ax}\, x^m\, {}_1F_1(p, m+1, qx)$

(*d*) The distribution (2·13) of Section 2.

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AN ELECTRICAL AIRPLANE C.G. POSITION INDICATOR*

By P. Nilakantan

Received November 10, 1945

Introduction

Although several types of Airplane C.G. Determinators are known which work on the mechanical principle of the lever just as the common balance, their manipulation is rather cumbersome and the devices themselves are not very handy. In the present paper an electrical circuit is described which is capable of indicating the centre of gravity position of an airplane for any arbitrary manner of loading after a few adjustments requiring very little skill. The design of the circuit for the case of a typical airplane is explained with the help of a numerical example. This should serve the purpose of further clarifying the theoretical considerations.

Basic Principle

The position of the centre of gravity of an airplane in the horizontal plane and at the normal attitude corresponding to the level flight condition at cruising speed, is determined by the relation,

$$x = \frac{\sum_{i=0}^{i=n} w_i x_i}{\sum_{i=0}^{i=n} w_i} = \frac{\sum_{i=0}^{i=n} m_i}{\sum_{i=0}^{i=n} w_i}, \qquad (1)$$

where w_i is the weight of load item i, and x_i is the corresponding moment arm measured from any convenient centre of gravity datum point, the total number of items being n. A simple electrical analogy of the division indicated in relation (1) may be envisaged by considering a voltage that is proportional to the algebraic sum of the moments, applied at the ends of a resistance that is proportional to the sum of the weights: the resulting current in the resistance will be proportional to the distance of the centre of gravity of the airplane from the datum point. This is the basic principle of the centre of gravity indicator.

Theory of the Electrical Circuit

The arrangement of an electrical circuit in order that the conditions mentioned above may be realized in practice is shown in Fig. 1.

* Patents applied for.

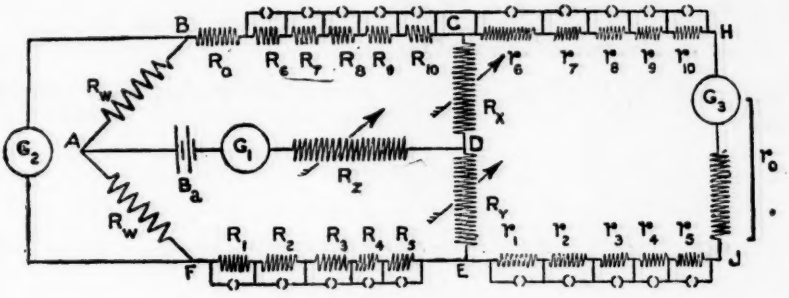

FIG. 1

The resistances, R_0, R_1, R_2,.... R_{10} shown in the figure, are made proportional to the moments m_0, m_1, m_2,.... m_{10} of the airplane weight empty and the altogether 10 items of the disposable load respectively (n is arbitrarily assumed to be 10 in this case). Similarly, the resistances r_0, r_1, ...r_{10} are made proportional to the corresponding weights w_0, w_1,.... w_{10} respectively. All the positive moments (clockwise) are included in the arm ABC while all the negative moments (anti-clockwise) are in the arm AFE of the electrical circuit. The R_w's are two equal resistances. G_1 and G_3 are current meters while G_2 is a sensitive galvanometer. G_2 has its zero reading in the middle of the scale.

The rheostats R_x and R_y may be so adjusted that G_2 reads zero: then the currents in the arms ABC and AFE are equal. The rheostat R_z could then be adjusted such that the current registered by G_1 has a specific value say c_1. c_1 is an instrument constant and its significance will become evident later. The currents in the arms ABC and AFE of the circuit will have the same value, say c_2, which again will be equal to $\frac{1}{2}c_1$. This is due to the fact that the two resistances R_w are equal and G_2 reads zero. The currents in the arms CD, DE. and CHJE will be equal to $c_2 + c_3$, $c_2 - c_3$, and c_3 respectively. Applying the well-known law of electrical networks, the following relations are obtained:—

$$c_2 R_A - c_2 R_B - c_3 r = 0 \qquad (2)$$

$$(c_2 + c_3) R_X - (c_2 - c_3) R_Y + c_3 r = 0 \qquad (3)$$

$$c_2 (R_w + R_A) + (c_2 + c_3) R_X = c_2 (R_w + R_B) + (c_2 - c_3) R_Y$$
$$= E_{Ba} - (R_{G1} + R_Z) c_1 = E \text{ say} \qquad (4)$$

where,

$$R_A = R_0 + R_6 + R_7 + R_8 + R_9 + R_{10},$$
$$R_B = R_1 + R_2 + R_3 + R_4 + R_5,$$
$$r = r_0 + r_1 + r_2 \ldots\ldots + r_{10};$$

R_{G_1} is the resistance of G_1 and

r_0 includes the resistance of G_3.

From equations (2), (3) and (4), the following relations are easily obtained, namely,

$$c_3 = \frac{(R_A - R_B)\, c_2}{r} \tag{5}$$

$$R_X = \left\{\frac{E}{c_2} - (R_w + R_A)\right\} \frac{r}{r + (R_A - R_B)} \tag{6}$$

$$R_Y = \left\{\frac{E}{c_2} - (R_w + R_B)\right\} \frac{r}{r - (R_A - R_B)} \tag{7}$$

Although the value of c_1 and therefore of c_2 also may be arbitrarily decided upon initially in order to suit the most advantageous design of the instrument, the absolute values of R_X and R_Y are not uniquely determined; their values will depend upon the values of E and R_w. The relative values of R_X and R_Y are, however, fixed by the values of R_A, R_B and r, according to the relation,

$$\frac{R_A - R_B}{r} = \frac{R_Y - R_X}{R_X + R_Y + r} \tag{8}$$

The operations performed may now be considered in the light of the above equations. The essential object of the manipulations has been to make c_2 equal to $\frac{1}{2}c_1$. The relation (5) then directly gives the answer to the problem. For, $(R_A - R_B)$ corresponds to the algebraic sum of the moments and r corresponds to the total weight of the airplane, c_2 being an instrument constant. Hence, c_3 is always proportional to $\frac{(R_A - R_B)}{r}$.

Assuming the resistances to be so chosen that 1 ohm of the resistances R_i is equivalent to a inch-pounds and that 1 ohm of the r_i's is equivalent to b pounds, we have then from equation (5),

$$\frac{c_3}{c_2} \cdot \frac{a}{b} = \frac{(R_A - R_B)\, a}{r \cdot b} \text{ inches.} \tag{9}$$

In other words, if c_3, read in milli-amperes, is multiplied by the factor $\frac{a}{b} \cdot \frac{1}{c_2}$ in which c_2 is also in milli-amperes, we get directly the C.G. position in inches from the datum point. For practical purposes G_3 can be calibrated in inches of C.G. position fore and aft. Since c_1 is an instrument constant, its value read on G_1 may also be indicated by an index mark on the dial of the instrument.

Some Practical Considerations

It is not the purpose here to go into minute details of design of the circuit for any airplane. But attention may be drawn to some points of practical interest by considering the case of a typical airplane of 6,000 lbs. gross weight. The weight and moment data of the airplane are given in Table I below.

Table I

Item	Weight W_i (lbs.)	Moment arm X_i (inches)	Moment m_i (inch—lbs.)
Airplane weight empty ..	4000	0	0
Pilot ..	170	−35	−5950
1st Passenger ..	170	− 5	− 850
2nd ,, ..	170	− 5	− 850
3rd ,, ..	170	25	4250
4th ,, ..	170	25	4250
5th ,, ..	170	55	9350
6th ,, ..	170	55	9350
Fuel (full) ..	450	10	4500
Cargo (full) ..	360	90	32400
Total ..	6000		56450

The datum point in the horizontal plane for the measurement of moment arms has been chosen for convenience as that corresponding to the centre of gravity position of the airplane weight empty. In fact, it may be preferable to choose the datum point given by the manufacturer himself and the centre of gravity limits specified in the *Airplane Manual* with reference to this datum point may be indicated on the dial of G_3. This however, is only a design detail.

Table II

Item No. i	Item Description	Resistances r_i (ohms)	Resistances R_i (ohms)
0	Airplane weight empty ..	400	0
1	Pilot ..	17	5·95
2	1st Passenger ..	17	·85
3	2nd ,, ..	17	·85
4	3rd ,, ..	17	4·25
5	4th ,, ..	17	4·25
6	5th ,, ..	17	9·35
7	6th ,, ..	17	9·35
8	Fuel ..	*0–45	*0–4 ·5
9	Cargo ..	*0–36	*0–32·4

* Adjustable in fractions $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$ of full value.

The electrical circuit for the airplane under consideration may be designed such that 1 ohm of the R_i's is equivalent to 1000 inch-pounds and 1 ohm of the r_i's to 10 pounds weight. The actual values of r_i and R_i for the various items are then as given in Table II.

The value of c_1 is fixed at 20 milli-amperes. Hence c_2 will be 10 milli-amperes. The multiplying factor is 10 when c_3 is read in milli-amperes, in order to get the C.G. position in inches. For the battery a two-volt accumulator cell may be used.

Considering the case of the fully loaded airplane, we have

$$R_A = 64{\cdot}1\ \Omega$$

$$R_B = 7{\cdot}65\ \Omega, \text{ and}$$

$$r = 600\ \Omega.$$

Hence $c_3 = {\cdot}941$ *m.a.* This evidently corresponds to a C.G. position of 9·41 inches aft of the datum point. If the R_w's are each equal to 10 Ω, then it may be easily shown that, corresponding to a value of $(R_{G_1} + R_Z) = 50\ \Omega$,

$$R_X = 23{\cdot}7\ \Omega, \text{ and}$$

$$R_Y = 90{\cdot}8\ \Omega,$$

from equations (4), (6) and (7).

It may also be shown that if R_X is initially kept at some arbitrary value, say 20 Ω, the appropriate values of R_Y and $(R_{G_1} + R_Z)$ are 86·48 Ω and 52 Ω respectively.

The above considerations show that the manipulation of the instrument is a very simple matter and often only R_Y and R_Z need be adjusted.

By means of the short-circuiting plugs provided, any arbitrary manner of loading of the airplane may be reproduced on the circuit (see Fig. 1), and the C.G. position in inches read directly on the dial of G_3 after two or three adjustments.

Summary

The theory of the electrical circuit of an Airplane C.G. Position Indicator has been developed. The practical application of the circuit to the case of a typical airplane has been demonstrated with the help of a numerical example.

THE ACTION OF HEXAMETHYLENE TETRAMINE ON PHENOLS AND THE METHYL ESTERS OF PHENOL CARBOXYLIC ACIDS

Part II. The Synthesis and Study of Methyl-2 : 3 : 4 Trihydroxy-5-formyl-benzoate

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2 : 4-Dihydroxy-5-formyl benzoic acid was synthesised by Desai and Radha,[1] by the action of hexamethylene tetramine on methyl-β-resorcylate in glacial acetic acid. The same reaction has now been extended to some phenols and to methyl-2 : 3 : 4-trihydroxy-benzoate.

Methyl-2 : 3 : 4- trihydroxy-benzoate on formylation with hexamethylene tetramine in glacial acetic acid, yielded methyl-2 : 3 : 4- trihydroxy-5-formyl-benzoate, which was characterized by the preparation of its 2 : 4-dinitrophenyl hydrazone, 4-nitrophenyl-hydrazone and semicarbazone derivatives.

The ortho-hydroxy-aldehydic structure of the formyl ester was proved by the preparation of the coumarin derivatives of the formyl ester with ethyl acetoacetate and ethyl malonate by the Knoevenagel condensation. Thus, with ethyl acetoacetate, the ester gave methyl-7 : 8-dihydroxy-3-acetyl-coumarin-6-carboxylate and with ethyl malonate, it afforded ethyl-7 : 8-dihydroxy-6-carbomethoxy coumarin-3-carboxylate.

Clemmensen reduction of the formyl ester afforded methyl-2 : 3 : 4-trihydroxy-5-methyl benzoate.

Hydrolysis of the ester gave the corresponding aldehydo-acid, 2 : 3 : 4-trihydroxy-5-formyl benzoic acid, which when subjected to decarboxylation underwent decomposition.

On Perkin's acetylation and condensation with bromacetic ester, the formyl ester was recovered unchanged.

Attempts were made to formylate orcinol, methyl-*p*-orsellinate, phloroglucinol, resacetophenone, methyl-resaceto-phenone carboxylate, hydroquinone, 1 : 3 : 5-triacetoxy benzene, methyl-α-resorcylate, γ-resorcylic acid, and methyl-γ-resorcylate. Of these, orcinol, methyl-*p*-orsellinate, phloroglucinol, γ-resorcylic acid and methyl-γ-resorcylate gave amorphous, yellowish-brown, high-melting compounds which contained appreciable amount

of nitrogen. Resacetophenone and hydroquinone gave oily products which did not solidify, whereas in the case of methyl resacetophenone carboxylate and 1:3:5-triacetoxy benzene, no reaction took place and the starting compounds were recovered. Methyl-α-resorcylate afforded a yellowish, nitrogenous amorphous, and high-melting compound which reacted with dinitrophenyl-hydrazine, indicating the presence of traces of the aldehyde compound.

Experimental

Formylation of methyl-2:3:4-trihydroxy benzoate: Methyl-2:3:4-trihydroxy-5-formyl benzoate. A mixture of methyl-2:3:4-trihydroxy benzoate (12 g.), hexamethylene tetramine (36 g.), glacial acetic acid (60 c.c.) and sodium bi-sulphite (6 g.) was heated on a water-bath for 8–10 hours and for further 3–4 hours after the addition of dilute hydrochloric acid (130 c.c., 1:1). An orange-red compound, which separated, was filtered off. The filtrate was salted and both the filtrate and the orange-red solid, were extracted with ether, when a pale-yellow mass was obtained on the evaporation of the ether. On crystallizing from dilute hot alcohol, whitish, shiny, micro-crystals were obtained (6·7 g.), m.p. 169–70°. (Found: C, 51·4; H, 4·3; $C_9H_8O_6$ requires C, 50·9; H, 3·8 per cent.) It gave a dark green colouration with alcoholic ferric chloride.

The 2:4-*dinitrophenyl hydrazone* of the formyl ester prepared in the usual manner and crystallized from glacial acetic acid in tiny orange-red crystals, melted at 295°. (Found: N, 14·2; $C_{15}H_{12}O_9N_4$ requires N 14·3 per cent.)

The 4-*nitrophenyl hydrazone* of the ester, prepared by the usual method and crystallized from acetic acid in orange red micro-crystals, melted at 285° with decomposition. (Found: N, 12·1, $C_{10}H_{12}O_4N_2$ requires N, 12·5 per cent.)

The semicarbazone of the ester, prepared in the usual manner, gave colourless micro-crystals, m.p. 238°. (Found: N, 15·6; $C_{10}H_{11}O_6N_3$ requires N, 15·7 per cent.)

Methyl-7: 8 dihydroxy-3-acetyl-coumarin-6-carboxylate.—Piperidine (3 drops) was added to a mixture of the formyl ester (1 g.) and ethyl acetoacetate (1 g.) dissolved in pyridine (10 c.c.), and the mixture was heated at 100° for one hour. The solid obtained on the addition of dilute hydrochloric acid was triturated with 2 N-potassium hydroxide solution to remove the unreacted formyl ester. The insoluble solid obtained crystallized in greyish-white needles from dilute hot alcohol, m.p. 263–64°. (Found: C, 56·3; H, 4·0; $C_{12}H_{10}O_7$ requires C, 56·1; H, 3·6 per cent.)

Ethyl-7: 8-dihydroxy-6-carbomethoxy-coumarin-3-carboxylate.—Piperidine (3 drops), was added to a mixture of the formyl ester (1 g.) and ethyl malonate (1 g.) dissolved in pyridine (10 c.c.) and the mixture was heated on boiling water-bath for two hours. The solid obtained on acidifying with dilute hydrochloric acid, crystallized from hot alcohol in colourless needles (0·25 g.), m.p. 245–47°. (Found: C, 54·2; H, 3·5; $C_{14}H_{12}O_8$ requires C, 54·5; H, 3·8 per cent.).

Methyl-2: 3: 4-trihydroxy-5-methyl benzoate.—The formyl ester (1·5 g.), dissoved in hot alcohol (20 c.c.), was gradually added to a mixture of zinc amalgam (prepared from 20 g. of zinc dust according to Robinson and Shah[2]) and dilute hydrochloric acid (50 c.c., 1: 1) at 100°, more alcohol being added to keep the ester in solution whenever it was necessary. After one hour, concentrated hydrochloric acid (10 c.c.) was added and the heating continued for a further half hour. The hot liquid, after filtration deposited shining, greyish micro-crystals, m.p. 178–79°, on cooling. The ethereal extract of the zinc amalgam gave a further yield of the same compound. Total yield (0·8 g.). (Found: C, 54·3; H, 5·0; $C_9H_{10}O_5$ requires C, 54·5; H, 5·0 per cent.) It did not react with 2: 4-dinitrophenyl hydrozine and the mixed melting point with the formyl ester was 130–40°.

2: 3: 4-*trihydroxy-5-formyl-benzoic acid.*—The aldehydo-ester (0·7 g.) was dissolved in sodium hydroxide solution (20 c.c., 10%) and heated on a water-bath for 2–3 hours. The hot solution was filtered and acidified with hydrochloric acid. The solid was purified through sodium-bi-carbonate solution and crystallized from very dilute alcohol in colourless micro-crystals, m.p. 221–22°, (Found: C, 48·7; H, 3·0; $C_8H_6O_6$ requires C, 48·5; H 3·0 per cent.)

The foregoing formyl acid (0·2 g.) was heated in a hard glass sealed tube with water (10 c.c.) and hydrochloric acid (1 c.c.) for 5–6 hours at 160–70°. The dark brown solid purified through sodium bicarbonate solution did not give tests for the aldehydo group with 2: 4-dinitro-phenyl-hydrazine.

Summary

1. Methyl-2: 3: 4-trihydroxy benzoate was formylated by the action of hexamethylene-tetramine in glacial acetic acid and methyl-2: 3: 4-trihydroxy-5-formyl benzoate was obtained. Several derivatives of the formyl ester were prepared and the structure established.

2. Formylation of several hydroxy compounds was also attempted.

References

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2. Robinson and Shah .. *J.*, 1934, 1497.

THE ACTION OF HEXAMETHYLENE TETRAMINE ON PHENOLS AND THE METHYL ESTERS OF PHENOL CARBOXYLIC ACIDS

Part III. The Synthesis and Study of Methyl-2-hydroxy-1-formyl-3-naphthoate

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In continuation of our previous work,[1] the formylation of phenols and phenol carboxylic esters, has now been extended to some methyl esters of naphthol-carboxylic acids, namely, methyl-2-hydroxy-3-naphthoate and methyl-2-hydroxy-1-naphthoate.

Methyl-2-hydroxy-3-naphthoate on formylation with hexamethylene tetramine in glacial acetic acid, yielded a mixture of methyl-2-hydroxy-1-formyl-3-naphthoate and 2-hydroxy-1-formyl-3-naphthoic acid. The structure of the latter was proved by the hydrolysis of the former and the subsequent hydrolysis product on decarboxylation underwent simultaneous deformylation to give β-naphthol. The formyl ester and the acid both were characterized by their functional derivatives, like 2:4-dinitro-phenyl hydrazones and semicarbazones. The ortho-hydroxy aldehydic structure was proved by the formation of coumarin derivatives, *viz.*, 3-acetyl-10 carbmethoxy-β-naphtha-α-pyrone and 3-carbethoxy-10-carbmethoxy-β-naphtha-α-pyrone by the knoevenagel condensation of the formyl ester with ethyl acetoacetate and ethyl malonate respectively. On subjecting it to Perkin's acetylation it yielded, 10-carbmethoxy-β-naphtha-α-pyrone while condensation with ethyl bromoacetate gave, ethyl-1-formyl-3-carbmethoxy-naphthalene-2 6-acetate, which on treating with sodium ethoxide in absolute alcohol, gave a coumarone derivative, ethyl-β-naphtha-furane-9-carboxy-2-carboxylate. Clemmensen reduction of the formyl ester with different solvents, under different conditions, gave different products. Methyl alcohol as the solvent afforded methyl-2-hydroxy-1-methyl-3-naphthoate, which on hydrolysis gave the corresponding acid, 2-hydroxy-1-methyl-3-naphthoic acid, which could not be decarboxylated.

However, when glacial acetic acid is used as the solvent and the reaction mixture heated for different lengths of time, two more compounds, which are being studied, are obtained.

Methyl-2-hydroxy-1-naphthoate could not be similarly formylated.

Experimental

Formylation of methyl-2-hydroxy-3-naphthoate.—Methyl-2-hydroxy-1-formyl-3-naphthoate and 2-hydroxy-1-formyl-3-naphthoic acid. A mixture of methyl-2-hydroxy-3-naphthoate (10 g.), hexamethylene tetramire (30 g.) and glacial acetic acid (50 c.c.) was refluxed on a water-bath for 5–6 hours and further for three hours, after the addition of hydrochloric acid (100 c.c., 1:1). The solid which separated was filtered, washed and treated with sodium bicarbonate solution (5%). The insoluble solid was washed with water and was crystallized from glacial acetic acid in very shiny, yellow plates, m.p. 146–47°. (Found: C, 67·6; H, 4·0; $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·3 per cent.) It gave an intense blue colouration with alcoholic ferric chloride.

The sodium bicarbonate-soluble portion was acidified with dilute hydrochloric acid, and the solid obtained was crystallized from very dilute alcohol in yellow micro-crystals, m.p. 218°–20°. Mixed melting point with 2-hydroxy-1-formyl-3-naphthoic acid (described later) was undepressed. (Found: C, 63·6; H, 4·0; $C_{12}H_8O_4$. $\frac{1}{2}H_2O$ requires C, 64·0; H, 4·0 per cent.). It gave effervescence with sodium bicarbonate solution and a blue colouration with alcoholic ferric chloride.

The p-*nitrophenyl-hydrozone* of the formyl ester prepared as usual, crystallized in orange-red microcrystals from glacial acetic acid, m.p. 295° (decomp.). (Found: N, 11·2; $C_{19}H_{15}O_5N_3$ requires, N, 11·5 per cent.)

The 2:4-*dinitrophenyl-hydrazone* prepared in the usual manner crystallized in orange-red crystals from glacial acetic acid, m. p. 298° (decomp.). (Found: N, 13·2; $C_{19}H_{15}O_5N_3$ required N, 13·6 per cent.)

The semicarbazone prepared as usual crystallized from alcohol in shiny, pale-yellow micro-crystals, m.p. 238°. (Found: N, 14·5; $C_{14}H_{13}O_4N_3$ requires N, 14·6 per cent.)

3-*carbethoxy*-10-*carbmethoxy*-β-*naphtha*-α-*pyrone.*—Piperidine (4 drops) was added to a mixture of the formyl ester (0·9 g.) and ethyl malonate (1 g.) dissolved in pyridine (10 c.c.) and the mixture was heated on a water-bath for two hours. The solid obtained on acidifying with hydrochloric acid was crystallized from hot alcohol in shiny, greenish-yellow micro-crystals, m.p.

157-58°. (Found: C, 66·2; H, 4·1; $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3 per cent.)

3-*Acetyl*-10-*carbmethoxy*-β-*naphtha*-α-*pyrone*.—A mixture of the formyl-ester (0·5 g.), ethyl acetoacetate (0·6 g.) and piperidine (3–4 drops) was heated on a water bath for two hours. During heating, very long yellow needles separated, which were filtered, washed with hydrochloric acid and water and dried, m.p. 240–41°. (Found: C, 68·6; H, 4·1; $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·0 per cent.).

Ethyl-1-*formyl*-3-*carbmethoxy*-*naphthalene*-2-o-*acetate*.—The formyl ester (0·9 g.) was dissolved in acetone (100 c.c.), ethyl bromo acetate (1 g.) and anhydrous potassium carbonate (2 g.) were then added to the mixture and refluxed on a water-bath for 10 hours. The excess of ethyl bromoacetate and acetone were driven off in a current of air, after filtering off the potassium carbonate, and the flaky mass obtained was crystallized from hot dilute alcohol in long, woolly, pale-yellow needles, m.p. 116–17°. (Found: C, 64·6; H, 4·7; $C_{17}H_{16}O_6$ requires C, 64·5; H, 5·0 per cent.)

Ethyl-β-*naphtha*-*furane*-9-*carboxy*-2-*carboxylate*.—The foregoing compound (1 g.) was dissolved in the minimum quantity of absolute alcohol (7 c.c.). Freshly cut metallic sodium (1 g.) was dissolved in absolute alcohol (25 c.c.) and was gradually added to the solution of the ester in small quantities with vigorous shaking. The flask was stoppered lightly and left for one hour at room temperature. The solution was filtered and acidified with hydrochloric acid. The yellow precipitate obtained crystallized in very shiny yellow, micro-crystals, m.p. 174–75°. (Found: C, 67·8; H, 4·5; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2 per cent.) It gave effervescence with sodium bicarbonate solution.

10-*Carbmethoxy*-β-*naphtha*-α-*pyrone*.—The formyl ester (1 g.) was heated on a sand-bath with acetic anhydride (20 c.c.) and anhydrous sodium acetate (2 g.) for 6 hours. The solid obtained was treated in the usual manner and crystallized from hot dilute alcohol in long golden yellow needles, m.p. 177°. (Found: C, 70·5; H, 3·5; $C_{15}H_{10}O_4$ requires C, 70·8; H, 3·9 per cent.)

Methyl-1-*methyl*-2-*hydroxy*-3-*naphthoate*.—The formyl ester (2 g.) dissolved in hot methyl alcohol was gradually added to a mixture of zinc amalgam, prepared from zinc dust (20 g.) according to Robinson and Shah[2] and dilute hydrochloric acid (50 c.c., 1 : 1) at 100°, more alcohol being added whenever necessary to keep the ester in solution. After one hour, concentrated hydrochloric acid (10 c.c.) was added and heating continued for a further half hour. The hot liquid was filtered, alcohol evaporated and the

acidic solution extracted with ether. The yellow solid obtained on the evaporation of ether crystallized from very dilute hot alcohol in long, pale yellow needles, m.p. 70–71°. (Found: C, 71·9; H, 5·5; $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·5 per cent.) It gave blue colouration with alcoholic ferric chloride, did not react with 2:4-dinitro-phenyl hydrazene, did not dissolve in nor gave effervescence with sodium bicarbonate solution.

Methyl-1-methyl-2-hydroxy-3-naphthoic acid.—Hydrolysis of the foregoing reduced ester by sodium hydroxide afforded a yellow solid, which on treating with sodium bicarbonate solution and subsequent acidification was finally obtained as a yellow solid which crystallized from hot dilute alcohol in very shiny yellow micro-crystals, m.p. 235°. (Found: C, 71·6; H, 4·9; $C_{12}H_{10}O_3$ requires C, 71·3, H, 4·9 per cent.) It sublimed on heating in a dry test-tube, gave effervescence with sodium bicarbonate solution and gave an intense blue colouration with alcoholic ferric chloride.

Clemmensen reduction of the formyl ester with glacial acetic acid as solvent.—The formyl ester (0·5 g.) was dissolved in glacial acetic acid and added to zinc amalgam prepared from zinc dust (15 g.) as usual. Concentrated hydrochloric acid (10 c.c.) was added to it and heated on a water-bath, the mixture being tested for the formyl group every five minutes with 2:4-dinitrophenyl-hydrazine. The heating was continued till the solution in the flask gave no precipitate with the hydrazine, which meant the completion of the reduction, and the solution was filtered hot. The filtrate deposited some pasty mass, which was purified and crystallized from hot dilute alcohol in shiny, yellow micro-crystals, m.p. 235°. This was identified as 1-methyl-2-hydroxy-3-naphthoic acid by the mixed melting point with the previously obtained acid in the last experiment.

The zinc amalgam was extracted with ether which on the evaporation gave a pasty mass and some yellow, crystalline solid. These were mechanically separated and the yellow crystals repeatedly crystallized from glacial acetic acid in shiny yellow micro-crystals, m.p. 223°. (Found: C, 73·6; H, 5·6.) It was insoluble in sodium hydroxide and sodium bicarbonate solutions. It did not give any colouration with alcoholic ferric chloride nor reacted with 2:4-dinitrophenyl hydrazene. The pasty mass on treating as usual with sodium bicarbonate solution and subsequent acidification, afforded 1-methyl-2-hydroxy-3-naphthoic acid, m.p. 235° which was identified by mixed melting point with the previously obtained acid.

The reduction experiment was repeated using glacial acetic acid as solvent, the heating being stopped after one hour.

The hot solution was filtered and deposited some yellow crystals, m.p. 250° and a pasty mass which were separated mechanically. The pasty mass on treating with sodium hydroxide solution and subsequent acidification gave 1-methyl-2-hydroxy-3-naphthoic acid, m.p. 255°. Mixed melting point with the previously obtained acid was undepressed.

The yellow crystals on repeated crystallization from glacial acetic acid gave yellow micro-crystals, m.p. 263–65°. (Found: C, 70·9; H, 5·1 per cent.) It dissolved neither in sodium hydroxide nor sodium bicarbonate solutions. It did not react with dinitrophenyl-hydrazine nor gave any colouration with alcoholic ferric chloride.

In another experiment, the reaction mixture was heated for 4 hours, and on giving the usual treatment, both the filtrate and the zinc amalgam yielded the product melting at 265°.

1-formyl-2-hydroxy-3-naphthoic acid.—The formyl ester (0·5 g.) was hydrolysed as usual, with alcoholic sodium hydroxide solution (10%). The solid obtained on acidifying the filtered alkaline solution, was washed and taken through sodium bicarbonate solution (5%) and filtered. On acidifying the filtrate with hydrochloric acid, a yellow solid was obtained which crystallized in shining yellow micro-crystals from hot alcohol, m.p. 222–23°. Mixed melting point with the previously obtained acid was unaltered. (Found: C, 63·6, H, 4·0; $C_{12}H_8O_4 + \frac{1}{2}H_2O$ requires C, 64·0, H, 4·0 per cent.)

Decarboxylation of the foregoing acid (0·3 g.) by heating it in a sealed carius tube with water (10 c.c.) and hydrochloric acid (1 c.c.) for 6–8 hours at 198–200° afforded a sticky paste. This, on triturating with sodium bicarbonate solution and filtration, left an insoluble pasty mass. This was washed with water and crystallized from boiling water in very lustrous, white silvery plates, m.p. 124–25°, and identified as β-naphthol.

The repetition of the experiment by heating the carius tube at a lower temperature and for a shorter time resulted in the formation of β-naphthol and some undecarboxylated acid.

Summary

1. Methyl-2-hydroxy-1-formyl-3-naphthoate was synthesised by the action of hexamethylene-tetramine on methyl-2-hydroxy-3-naphthoate.

2. Similar formylation of methyl-2-hydroxy-1-naphthoate was attempted with negative results.

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THE ACTION OF HEXAMETHYLENE TETRAMINE ON PHENOLS AND THE METHYL ESTERS OF PHENOL CARBOXYLIC ACIDS

Part IV. The Synthesis and Study of Methyl-1-hydroxy-4-formyl-2-naphthoate and 2-Acetyl-4-formyl-α-naphthol

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IN continuation of the previous work[1] the formylation of phenols and phenol-carboxylic esters has now been extended to methyl-1-hydroxy-2-naphthoate, 2-acetyl-α-naphthol and 4-acetyl-α-naphthol.

Methyl-1-hydroxy-2-naphthoate on formylation with hexamethylene tetramine in glacial acetic acid, yielded a mixture of methyl-1-hydroxy-4-formyl-2-naphthoate and 1-hydroxy-4-formyl-2-naphthoic acid. The structure of the latter was established by the hydrolysis of the former. The formyl ester and acid both were characterized by their functional derivatives, like 2:4-dinitrophenyl hydrazones and semicarbazones. Clemmensen reduction of the formyl ester afforded methyl-1-hydroxy-4-methyl-naphthoate, which on hydrolysis gave the corresponding acid. This acid on decarboxylation yielded the known 4-methyl-α-naphthol of Lesser[2] which proved the 4-position of the formyl group and the structure of the formyl ester.

The formyl ester with ethyl aceto-acetate, ethyl malonate and ethyl-bromo-acetate afforded, 3-carbmethoxy-4-hydroxy-naphthylidene ethyl-aceto-acetate, 3-carbmethoxy-4-hydroxy-napthylidene ethyl malonate and ethyl-4-formyl-2-carbmethoxy naphthalene 1-*o*-acetate respectively. On Perkin's acetylation the hydroxyl group got acetylated and methyl-1-acetoxy-4-formyl-2-naphthoate was obtained.

2-acetyl-α-naphthol on similar formylation afforded 2-acetyl-4-formyl-α-naphthol. The formyl ketone did not undergo Knoevenagel condensation with ethyl acetoacetate and ethyl malonate, nor did it condense with ethyl bromo acetate. When subjected to Perkin's acetylation the ketone was recovered and Clemmensen reduction gave an oil which would not solidify.

The formyl ketone was characterized by the preparation of 2:4-dinitrophenyl-hydrazone and semicarbazone.

4-Acetyl-α-naphthol, could not be similarly formylated and the original ketone was recovered quantitatively.

Experimental

Formylation of methyl-1-hydroxy-2-naphthoate: Methyl-1-hydroxy-4-formyl-2-naphthoate and 1-hydroxy-4-formyl-2-naphthoic acid.—A mixture of methyl-1-hydroxy-2-naphthoate (10 g.), hexamethylene tetramine (30 g.) and glacial acetic acid (50 c.c.) was refluxed on a water-bath for 5–6 hours and further half an hour more after the additon of dilute hydrochloric acid (50 c.c., 1 : 1). The solid that separated was filtered, washed and taken through sodium bicarbonate solution (5 per cent.). The insoluble solid was washed with water and was crystallized from hot dilute alcohol in long golden yellow needles, m.p. 123–24°. (Yield, 4·5 g.) Recrystallization from glacial acetic acid gave very shiny, yellowish brown plates, m.p. 126–27°. (Found: C, 68·4; H, 4·8; $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·4 per cent.) It gave a bluish purple colouration with alcoholic ferric chloride.

The sodium bicarbonate-soluble portion was obtained by acidifying the filtrate with dilute hydrochloric acid. The solid obtained was washed and crystallized from very dilute alcohol in yellow, micro-crystals (0·98 g.) m.p. 250°. Mixed melting point with 1-hydroxy-4-formyl-2-naphthoic acid (described later) was undepressed. It gave effervescence with sodium bicarbonate solution and reacted with 2: 4-dinitrophenyl hydrazine and semicarbazide.

The formylation did not succeed if the methyl ester was replaced by the acid. The reaction gave a complex, yellow, nitrogenous and high-melting compound.

The 2: 4-*dinitrophenyl-hydrazone*, prepared as usual, crystallized in orange needles from glacial acetic acid, m.p. 267–69°. (Found: N, 13·4, $C_{19}H_{14}O_7N_4$ requires N, 13·7 per cent.)

The 4-*nitrophenyl-hydrazone*, prepared in the usual manner crystallized in orange-red needles from acetic acid, m.p. 267–68°. (Found: N, 11·3; $C_{19}H_{15}O_6N_3$ requires N, 11·5 per cent.)

The semicarbazone, prepared as usual, crystallized in shining pale yellow, microcrystals, from alcohol, m.p. 275°. (Found: N, 14·4; $C_{14}H_{13}O_4N_3$ requires N, 14·6 per cent.).

3-*Carbmethoxy*-4-*hydroxy-napthylidene aceto-acetate.*—Piperidine (4 drops) was added to a mixture of methyl-1-hydroxy-4-formyl-2-naphthoate (2 g.) and ethyl acetoacetate (2 g.), dissolved in pyridine (10 c.c.). The

mixture was heated on a boiling water-bath for 2 hours. The solid obtained on acidification with hydrochloric acid, was crystallized from hot alcohol in colourless tiny needles, m.p. 133–34°. Mixed melting point with the formyl ester was 95–118°. (Found: C, 66·4; H, 5·3; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3 per cent.).

3-*Carbmethoxy-4-hydroxy-naphthylidene-ethyl-malonate.*—Piperidine (3 drops) was added to a mixture of the formyl ester (2 g.) and ethyl malonate (2 g.) dissolved in pyridine (10 c.c.). The mixture was heated on a water bath for 2 hours and the solid obtained on acidifying it with hydrochloric acid, crystallized from alcohol in colourless tiny needles, m.p. 142–43°. (Found: C, 64·1; H, 5·5; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·3 per cent.)

Ethyl-4-formyl-2-carbmethoxy-naphthalene-1-o-acetate.—To a solution of the formyl ester (1 g.) in dry acetone (100 c.c.), ethyl bromo-acetate (1·5 c.c.) and anhydrous potassium carbonate (2 g.) were added. The mixture was well shaken and refluxed on a water-bath for 10 hours. The excess of brom-acetic ester and acetone were driven off in a current of air, after filtering off the potassium carbonate. The white solid obtained, was crystallized in pale-yellow micro-crystals from hot alcohol, m.p. 205–06°. (Found: C, 64·7; H, 5·5; $C_{17}H_{16}O_6$ requires C, 64·5; H, 5·0 per cent.)

Methyl-1-acetoxy-4-formyl-2-naphthoate.—The formyl ester (1 g.) was heated with acetic anhydride (10 c.c.) and anhydrous sodium acetate (1 g.) on a sand-bath for 6–7 hours. The solid obtained was worked up as usual and crystallized from dilute hot alcohol in colourless, shiny, micro-crystals, m.p. 182–83°. (Found: C, 59·1; H, 5·2; $C_{15}H_{12}O_5 + H_2O$ requires C, 58·8; H, 5·2 per cent.)

Methyl-1-hydroxy-4-methyl-2-naphthoate.—The formyl ester (2 g.), dissolved in hot alcohol, was gradually added to a mixture of zinc amalgam prepared from zinc dust (15 g.), according to Robinson and Shah[3] and dilute hydrochloric acid (50 c.c., 1 : 1) at 100°, more alcohol being added whenever necessary to keep the ester in solution. After 1 hour, concentrated hydrochloric acid (10 c.c.) was added and heating continued for a further half hour. The hot filtrate, on cooling, deposited long, pinkish, shiny micro-crystals, m.p. 109–10°. (Found: C, 72·3; H, 5·3; $C_{13}H_{12}O_3$ requires C, 12·2; H, 5·5 per cent.)

1-*Hydroxy-4-methyl-2-naphthoic acid.*—The foregoing reduced ester (0·5 g.) was hydrolysed in alcoholic alkaline solution as usual. The solid obtained on acidification with hydrochloric acid was taken through sodium bicarbonate solution (5%), filtered and again acidified with dilute hydrochloric acid. The

solid obtained crystallized from very dilute alcohol in pinkish micro-crystals, m.p. 209–10°. (Found: C, 71·0; H, 4·8. $C_{12}H_{10}O_3$ requires C, 71·3; H, 4·9 per cent.) *Decarboxylation* of 1-hydroxy-4-methyl-2-naphthoic acid (0·5 g.) by heating with acidulated water (10 c.c.) in a sealed carius tube for 6–8 hours at 180–90°, gave a black solid. This was triturated with sodium bicarbonate solution and the insoluble solid crystallized from boiling water in long, pinkish needles, m.p. 86–87°. This was identified as 4-methyl-α-naphthol by a mixed m.p. with an authentic specimen.

1-*Hydroxy-4-formyl-2-naphthoic acid.*—Methyl-1-hydroxy-4-formyl-2-naphthoate (0·5 g.) was dissolved in sodium hydroxide solution (20 c.c., 10%) and heated on a water bath for 2 hours. The solution was filtered and acidified with hydrochloric acid. The pale yellow solid obtained was washed and crystallized from hot dilute alcohol in pale yellow woolly needles, m.p. 250–52°. Mixed melting point with the previously obtained acid was undepressed. (Found: C, 66·6; H, 4·1; $C_{12}H_8O_4$ requires C, 66·6; H, 3·7 per cent.) It gave effervescence with sodium bicarbonate solution and bluish-purple colouration with alcoholic ferric chloride.

Decarboxylation of the foregoing formyl acid (0·5 g.) by heating it with water (10 c.c.) and hydrochloric acid (1 c.c.) in a sealed carius tube 160–80° for 6–8 hours, gave a solid which on treating in the usual way afforded a compound which crystallized in very long, pinkish needles from hot water, m.p. 95–97°, and the mixed melting point with an authentic specimen of α-naphthol was undepressed.

Formylation of 2-acetyl-α-naphthol. 2-Acetyl-4-formyl-α-naphthol.—A solution of dry 2-acetyl-α-naphthol (10 g.), hexamethylene tetramine (30 g.) in glacial acetic acid (50 c.c.) was first heated on a water-bath for 3–4 hours and then refluxed on a sand-bath for 3 hours and further heated for 3 hours on a water-bath after the addition of hydrochloric acid (100 c.c., 1 : 1).

The solid which separated out in very fine long needles, was filtered, washed and crystallized from glacial acetic acid in long golden yellow needles, m.p. 154–55°. The acidic filtrate yielded some more of the compound on extraction with ether. Total yield (3·3 g.). (Found: C, 72·6, H, 4·4; $C_{13}H_{10}O_3$ requires C, 72·9; H, 4·6 per cent.) The formyl compound was fairly soluble in alkali and with alcoholic ferric chloride, it gave a dark-green colouration. It was very soluble in alcohol, acetone and fairly soluble in acetic acid from which it was crystallized.

The 4-nitrophenyl-hydrazone prepared in the usual manner, crystallized from glacial acetic acid in orange-red micro-crystals, m.p. 295° (decomp.). (Found: N, 11·8; $C_{19}H_{15}O_4N_3$ requires N, 12·0 per cent.)

The 2:4-*dinitrophenyl hydrozone* prepared as usual crystallized in small shiny micro-crystals from acetic acid, m.p. 285° (decomp.). (Found: N, 14·1; $C_{19}H_{14}O_6N_4$ requires N, 14·2 per cent.).

The semicarbazone, prepared as usual, gave pale yellow shining micro-crystals from boiling alcohol, m.p. 298° (decomp.). (Found: N, 15·3; $C_{14}H_{13}O_3N_3$ requires N, 15·5 per cent.).

Summary

Methyl-1-hydroxy-4-formyl-2-naphthoate and 2-acetyl-4-formyl-α-naphthol have been synthesised by the action of hexamethylene tetramine in glacial acetic acid, on methyl-1-hydroxy-2-naphthoate and 2-acetyl-α-naphthol respectively.

Similar formylation of 4-acetyl-α-naphthol did not succeed.

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2. Lesser, A. .. 402, 24.
3. Robinson and Shah, J. .. 1934, 1497.

SYNTHESIS AND STUDY OF 5:6:7:8-HYDROXY-FLAVONOLS

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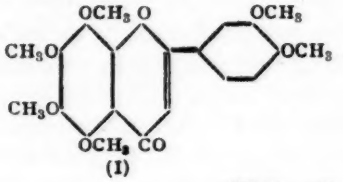
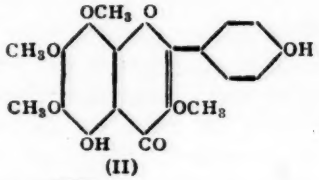
Flavones and flavonols with hydroxyl groups in all the four positions, 5, 6, 7 and 8, seem to be more widely occurring in nature than originally expected. They are, however, recent discoveries and they do not occur free as such, but are found to be partially or completely methylated. Nobiletin (I) is a fully methylated flavone of this type and it was isolated by Tseng[1] from the peels of the Chinese Mandarian oranges (*Citrus nobilis*). Robinson and Tseng[2] established its constitution as 5:6:7:8:3′:4′-hexamethoxy flavone. It has recently been synthesised by Horii[3] by the condensation of 2-hydroxy-3:4:5:6-tetramethoxy-acetophenone with veratroyl chloride and the conversion of the product into the flavone according to the method of Baker and Venkataraman. Calycopterin (II) is a partially methylated flavonol, isolated earlier by Ratnagiriswaran, Sehra and Venkataraman[4] from the coppered coloured leaves of *Calycopteris floribunda*. It was also found to be present in the leaves of *Digitatis thapsi* (Spanish digitalis) by Karrer[5] and hence called also by the name thapsin. Its constitution has been recently given as 5:4′-dihydroxy-3:6:7:8-tetramethoxy-flavone (II)[6]. Erianthin (III) is also considered to be a flavonol of this series; it is partially methylated and has been recently obtained from the plant, *Blumea eriantha* D.C. by Bose and Dutt.[7]



(I)



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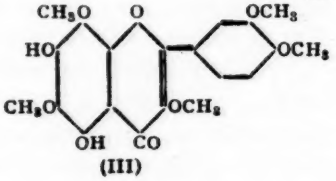
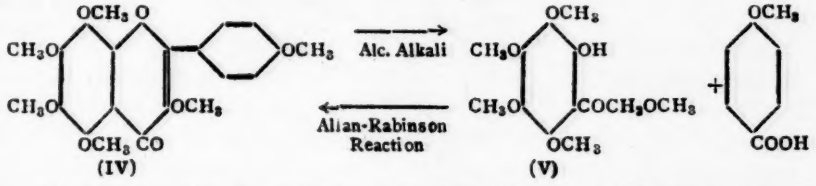


(III)

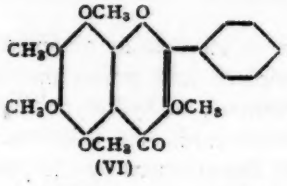
So far these are the only compounds that have been studied in detail. Some other substances isolated in this laboratory seem also to belong to this group. Full information is not available about these compounds enabling the identification of new members easy and this is particularly necessary since frequently these substances could be isolated only in very small quantities. A more detailed study of the hexahydroxy-flavone, calycopteretin, has therefore been made now. Further, other members of this flavonol group have also been prepared and their reactions and derivatives studied in detail.

The dimethyl ether of calycopterin is more easily obtained pure by methylating calycopterin with dimethyl sulphate and potassium carbonate in anhydrous acetone solution. When subjected to hydrolytic fission with 8% absolute alcoholic potash, it yields, besides anisic acid, a ketonic product as a low melting solid which could also be characterised by the preparation of the 2:4-dinitrophenyl-hydrazone. Analytical data of these two substances and reactions show that the ketone is 2-hydroxy-ω: 3:4:5:6-pentamethoxy-aceto-phenone (V). Condensation of the ketone with anisic anhydride and sodium anisate yields dimethyl calycopterin. These experiments confirm the results of previous workers[4,5,6] that calycopterin is a tetramethyl ether of 3:5:6:7:8:4′-hexahydroxyflavone.



Starting from the above ketone the other members of this flavonol group have been obtained. The following is a brief account of the results. The ketone condensed with benzoic anhydride and sodium benzoate smoothly yielding 3:5:6:7:8-pentamethoxyflavone (VI) as the sole product. On demethylation the corresponding penta-hydroxy compound, 6:8-dihydroxy-galangin (VII) was obtained. By the condensation of the abovementioned ketone with the anhydride and sodium salt of veratric acid, two products were isolated, one of which separated out from alkaline solution and consisted essentially of the normal hepta-methoxy flavone (VIII) and the other separated from the solution after saturation with carbon-dioxide and consisted mainly of the partially demethylated product (IX) showing the properties of a free hydroxyl in the 5-position. Examination of these revealed that they were still mixtures with indefinite melting points and purification

could not be achieved satisfactorily. However by methylating them a pure sample of the hepta-methoxy flavone (VIII) and by demethylating them the corresponding hepta-hydroxy flavone, 6 : 8-dihydroxyquercetin (X) were readily obtained. A pure sample of 5-hydroxy-3 : 6 : 7 : 8 : 3′ : 4′-hexamethoxyflavone (IX) could, however, be obtained by ether-extracting the aqueous mother-liquor after the filtration of the impure sample of (IX) that first separated out. It gave a prominent ferric chloride colour and a sparingly soluble potassium salt when treated with alcoholic potash.



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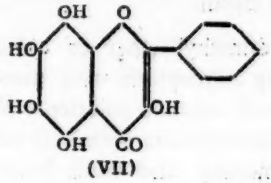

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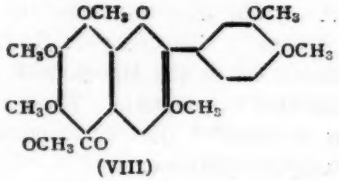

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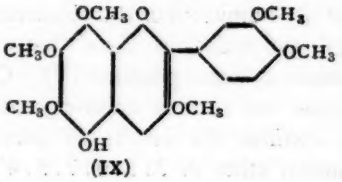

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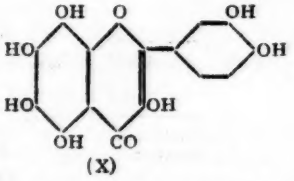
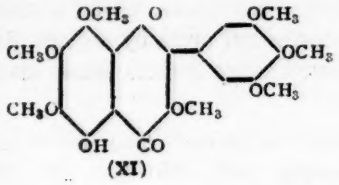


(X)

According to Bose and Dutt[7] methyl erianthin should be identical with the abovementioned 5-hydroxy-hexamethoxy flavone (IX). But the recorded properties are not the same. Methyl erianthin is reported to crystallise in the form of needles and melt at 141°. The above hydroxy flavone (IX) crystallises in the form of plates and melts at 122°. The lower melting point of compound (IX) may be considered to be genuine from a comparison of analogous 5-hydroxy-compounds and the related fully methylated flavonols given in Table I. For example, monomethyl calycopterin melts at 124° whereas the dimethyl ether melts at 134°. The 5-hydroxy-compound (XI) described later on also melts 10° lower then the fully methylated ether.

When the anhydride and the sodium salt of trimethyl-gallic acid were used for the above Allan-Robinson condensation the product consisted entirely of the 5-hydroxy compound (XI). The octamethoxy flavone (XII)

was obtained from it by methylation and the octahydroxy compound (XIII), 6 : 8-dihydroxymyricetin by demethylation. This is the most highly hydroxylated compound of the flavone group known so far and is thus of special interest.



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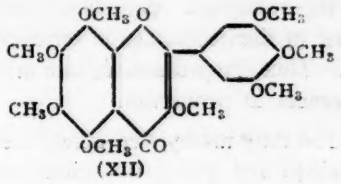

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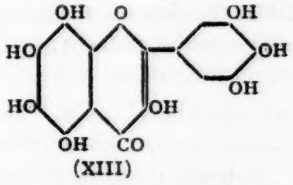

(XIII)

For the purpose of conveniently naming them, the new flavanols are considered to be derived from the series, galangin, kæmferol, quercetin and myricetin which have the 5 : 7-arrangement of hydroxyl groups and which seem to be more fundamental in evolution giving rise to the others by oxidation of the nuclear positions concerned.

The above hydroxyflavonols are in general yellow crystalline substances, the colour changing to green on storage. While 6 : 8-dihydroxygalangin is the most stable, retaining its yellow colour for several months, the others change from yellow to greenish yellow and green, the rapidity of the change reaching the maximum with the octa-hydroxy compound, 6 : 8-dihydroxy-myricetin. With water, even in the cold, they give a green colour and on boiling, the colour intensifies to deeper green or blue. Even an alcoholic solution changes colour from yellow to green and blue on standing or heating. Crystallisation of the flavonols should not be done with solvents like alcohol and acetic acid and it is best effected by using pure dry ethyl acetate. The pure substances do not exhibit any fluorescence in alcoholic solution or even in concentrated sulphuric acid. Like most hydroxy-flavonols they all give bright red colour when treated with magnesium and hydrochloric acid in alcoholic solution.

The new series of flavonols can be viewed in two ways, (1) as 5 : 7 : 8-hydroxyflavonols with an additional hydroxyl group in the 6-position and (2) as 5 : 6 : 7-hydroxy flavonols with an additional hydroxyl group in the 8-position. In conformity with the first point of view, they exhibit colour

changes in alkaline solutions more remarkable than the members of the gossypetin series. These have been studied in detail using buffer solutions and the results may be useful for purposes of identifying samples. But they do not react with *p*-benzoquinone in the manner characteristic of gossypetin and its analogues. Bargellini's test yielding green flocks, which is characteristic of the quercetagetin series of flavonols is not given by the new flavonols. Thus the presence of one more hydroxyl group in them causes marked differences in properties.

The fully methylated ethers are colourless substances, insoluble in aqueous alkali and giving no colour with alcoholic ferric chloride. The ethers which have a free hydroxyl in the 5-position dissolve in aqueous alkali only with difficulty, form sparingly soluble potassium salts with alcoholic potash and give prominent ferric chloride colour.

The acetates are also colourless solids. Their crystallisation from boiling alcohol seems to bring about partial hydrolysis and the products assume colour on storage. It should therefore be carried out using anhydrous solvents or in the cold using acetone-alcohol mixture.

Table I gives some of the important data relating to this new series of flavonols and their derivatives.

TABLE I

Flavonols	6 : 8-Dihydroxy-galangin	Calycopteretin	6 : 8-Dihydroxy-quercetin	6 : 8-Dihydroxy-myricetin
1. Alc. $FeCl_3$ ..	Olive green changing to brown	Bright green changing to brown	Deep green changing to brown	Deep green changing to brown
2. Mg+HCl ..	Orange red	Red	Deep red	Deep red
3. M.p. of the flavonols	257–58° (with decom.)	318–20° (with decomp.)	Turns dark above 300; does not melt below 360°	Turns dark above 300°; does not melt below 360°
4. M.p. of the acetates	201–03°	218–20°	221° with sintering at 219°	225° with sintering 221°
5. M.p. of the fully methylated ethers	80–82°	133–34° 131° (Shah *et al*[6])	129–31°	122–23°
6. M.p. of partial methyl ethers with the 5-hydroxyl alone free	..	124° (Shah *et al*[6])	122–23°	113–15°

EXPERIMENTAL

Methylation of calycopterin : Dimethylcalycopterin (IV).—

Calycopterin (1·0 g.) was dissolved in dry acetone (25 c.c.), treated with dimethyl sulphate (1·0 c.c.) and anhydrous potassium carbonate (10·0 g.)

and boiled under reflux for a period of 20 hours. The solvent was then removed by distillation and the residue treated with water (150 c.c.). The methyl ether soon separated out. On crystallisation from alcohol, it came out in sheaves of colourless elongated needles melting at 133–34° (*Cf.* Shah *et al.*,[6] pale yellow needles, m.p. 131°) and did not dissolve in aqueous alkali. (Found: C, 62·9; H, 5·7; OCH_3, 46·0; $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5; OCH_3, 46·2%.) Yield, 1·0 g.

Decomposition of the methyl ether with alcoholic potash : Isolation of anisic acid and ketone (V).—

Dimethyl calycopterin (1·0 g.) was boiled under reflux with 8% absolute alcoholic potash (30 c.c.) for a period of six hours. At the end of this period, as much of the alcohol as possible was removed by distillation and the residue dissolved in water. The solution was filtered from any suspended impurities, and then acidified with dilute sulphuric acid. The precipitated crystalline solid was filtered, washed with cold water and then crystallised from boiling water when it came out as colourless rectangular plates and prisms melting at 185°. It was found to be anisic acid. The mixed melting point with an authentic sample of anisic acid was undepressed. The filtrate was repeatedly ether-extracted and the combined ether solution washed with sodium bicarbonate solution (5%) to remove completely the acid part. The ether solution was then washed with water and the solvent evaporated. The residue was a pale yellow liquid which solidified on keeping in an ice-chest for a number of days. It crystallised from petroleum ether (b.p. about 60°) as pale yellow rectangular plates and prisms melting at 65–67° (Karrer[5] gives mp. 66–67°). It gave a green colour with alcoholic ferric chloride. Yield, 0·38 g. (Found: C, 54·8; H, 6·1; OCH_3, 53·9; $C_{13}H_{18}O_7$ requires C, 54·6; H, 6·3; OCH_3, 54·2%.) The ketone was also characterised as its 2 : 4-*dinitrophenylhydrazone* in the following manner:

The ketone (0·2 g.) dissolved in alcohol (2 c.c.) was treated with 2 : 4-dinitrophenylhydrazine (0·2 g.) in alcohol (2·0 c.c.). The clear solution was then boiled under reflux on a water-bath for ½ hour. On cooling the alcoholic solution, the phenylhydrazone separated out. In was filtered and crystallised from dilute alcohol when it came out as short orange red rectangular prisms melting at 174–75°. (Found: C, 45·2; H, 5·0; OCH_3, 31·1; $C_{19}H_{22}O_{10}N_4$, $2H_2O$ requires C, 45·4; H, 5·2; OCH_3, 30·9%.) Loss on drying could not be estimated as the substance sublimed easily above 100° *in vacuo*.

Synthesis of dimethyl calycopterin (IV).—

An intimate mixture of sodium anisate (2 g.), anisic anhydride (4·0 g.) and the ketone (V) (0·75 g.) was heated in an oil-bath at 180° *in vacuo* for a

period of five hours. The hard mass was then broken up and dissolved in alcohol (50 c.c.). To the solution boiling under reflux was added aqueous potassium hydroxide solution (5 g. in 10 c.c. of water) during the course of half an hour and the boiling continued for another half-hour in order to decompose completely the unreacted anhydride. The alcohol was then removed by distillation under reduced pressure and the residue treated with excess of water. The methyl ether separated out as long needle-shaped colourless crystals. It was filtered and the product was crystallised from dilute alcohol when it came out as sheaves of colourless elongated needles melting at 133–34°. The mixed melting point with the sample obtained directly from calycopterin by methylation was undepressed. Yield, 0·5 g.

The clear alkaline solution from which the hexamethyl ether had separated out was then saturated with carbon dioxide. No product was obtained even by ether extraction.

Demethylation of Calycopterin: Calycopteretin (6 : 8-*dihydroœy-kœmpferol*).

Calycopterin (0·5 g.) was dissolved in acetic anhydride (10·0 c.c.) and treated with hydriodic acid (10·0 c.c.; d. 1·7) with cooling. The clear solution was then boiled under reflux for half an hour, poured into ice-water and iodine present decomposed by passing sulphur-dioxide gas. The precipitated flavonol was twice recrystallised from ethyl acetate when it came out as bright yellow short rectangular plates, melting with decomposition at 318–20°. When crystallised from acetic acid it came in the form of golden yellow needles which soon turned green on exposure to air. (Found: C, 56·8; H, 3·4; $C_{15}H_{10}O_8$ requires C, 56·6; H, 3·2%.) It gave a bright green colour with alcoholic ferric chloride which rapidly changed to brown. The flavonol exhibited a series of colours in alkaline solution, the precise variations depending on the conditions of the reaction. Thus with 5% sodium bicarbonate it slowly dissolved to give a yellowish green and then green colour changing to greenish-blue and blue; it faded after 10 minutes to light green with a green precipitate. With 5% sodium carbonate the colours were yellow and deep green, quickly becoming blue on shaking; it then faded and became yellowish green within two minutes, brownish yellow and finally brown. With 5% caustic alkali the solution was reddish brown changing to red.

Calycopterin-hexaacetate.—

A small quantity of the flavonol was acetylated using acetic anhydride and a drop of pyridine and boiling for one hour. The product was then crystallised from cold acetone solution enough ethyl alcohol being added just to start the crystallisation. It came out as colourless needles melting at

218–20°. (Found: C, 56·9; H, 4·1; $C_{27}H_{22}O_{14}$ requires C, 56·8; H, 3·9%.)

Condensation of the ketone (V) with benzoic anhydride and sodium benzoate; preparation of pentamethoxy flavone (VI).—

An intimate mixture of benzoic anhydride (10 g.), sodium benzoate (2 g.) and the ketone (0·75 g.) was heated at 175–80° for a period of 5 hours. The product melted completely within the first one hour and later solidified. The reaction mixture was broken up in alcohol (50 c.c.) and while boiling under reflux, a solution of potassium hydroxide (15 g. in 25 c.c.) was added during the course of 20 minutes. The solution was boiled for a further 20 minutes to decompose the anhydride. The alcohol was then removed under reduced pressure and the residue treated with water. A viscous liquid separated out which did not solidify easily. Hence, the mixture was ether extracted, and the ether extract washed with water to remove alkali. After distilling off the solvent, the product was purified by dissolving in acetone and adding petroleum ether when coloured impurities separated out. The clear solution was then decanted; evaporation of the solvent left a viscous liquid which solidified during the course of 24 hours on keeping in an ice-chest. The product was further purified by crystallisation from dilute methyl alcohol when it came out as colourless rectangular prisms melting at 80–82°. It was insoluble in dilute alkali and did not give any colour with ferric chloride. (Found: C, 64·6; H, 5·3; $-OCH_3$, 41·6; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4; $-OCH_3$, 41·7%.) Nothing was obtained on saturating the aqueous alkaline solution with carbon dioxide and extracting with ether.

6 : 8-*Dihydroxy-galangin (VII).—*

The methyl ether (0·5 g.) obtained above was demethylated according to the procedure described for calycopterin. The crude product came out as shining yellow needles. It was unaffected by water at ordinary temperature but on heating the solution turned green. Two crystallisations from ethyl acetate yielded yellow rectangular plates melting at 257–58°. It did not change colour on exposure to air. With alcoholic ferric chloride, it gave an olive green colour changing to brown. On treatment with concentrated sulphuric acid, the crystals turned orange red, later on dissolving to give a yellow solution. It did not exhibit any fluorescence in daylight. (Found: C, 59·3; H, 3·6; $C_{15}H_{10}O_7$ requires C, 59·6; H, 3·3%.) Yield 0·3 g. The flavanol exhibited the following colour changes in alkaline solution. With 5% sodium bicarbonate, the substance dissolved slowly to form a deep blue solution with a violet tinge which started fading after 12 minutes giving a green precipitate; with 5% sodium carbonate, it gave

immediately a blue colour and faded very fast to yellow and then to pale yellow. With caustic alkali, it immediately formed a reddish brown solution; on shaking with air it rapidly became yellow, yellowish green and finally yellow.

The flavonol (VII) was acetylated using acetic anhydride and one drop of pyridine. The acetate was purified by crystallisation from acetone-ethyl alcohol mixture as described previously when it came out in the form of colourless needles and rectangular plates melting at 201–03°. (Found: C, 58·7; H, 4·0; $C_{25}H_{20}O_{12}$ requires C, 58·6; H, 3·9%.)

Condensation of the ketone (V) with veratric anhydride and sodium veratrate.—

An intimate mixture of veratric anhydride (4 g.) and sodium veratrate (2 g.) and the ketone (0·75 g.) was heated *in vacuo* at 175–80° for a period of 5 hours. The product melted and formed a reddish-brown liquid which soon solidified. After the reaction was complete, it was broken up in alcohol (50 c.c.) and while boiling under reflux a solution of potassium hydroxide (5 g.) in 10 c.c. was added during the course of 20 minutes. The alcohol was then removed under reduced pressure and the residue dissolved in water. The product (A) that separated out was filtered and the clear filtrate was saturated with carbon dioxide when a yellow solid (B) separated out. (A) melted between 108 and 118° and (B) between 115 and 123°. Purification by fractional crystallisation from alcohol could not be effected successfully as the fractions continued to melt indefinitely and hence product (A) was directly used for complete methylation and product (B) for demethylation.

5-*Hydroxy-hexamethoxyflavone* (IX).—

The mother-liquor was extracted twice with ether and on evaporating the solvent, a viscous residue was obtained which solidified on cooling. It was crystallised from dilute alcohol when it appeared as yellow rectangular plates melting 122–23° (*cf.* methyl erianthin,[7] yellow needles, m.p. 141°). It appeared to be exclusively the 5-hydroxy compound from the sharpness of its melting point. It gave a green colour with ferric chloride and formed a sparingly soluble potassium salt in alcoholic potash. Though it did not dissolve easily in cold aqueous potash, it did so on warming and formed a yellow solution. (Found: C, 60·5; H, 5·5; OCH_3, 44·7; $C_{21}H_{22}O_9$ requires C, 60·3; H, 5·3; OCH_3, 44·5%.) Yield, 90 mg.

3:5:6:7:8:3′:4′-*Heptamethoxy-flavone* (*VIII*).—

Product (A) obtained from the above condensation was directly methylated using dimethyl sulphate and potassium carbonate in acetone solution. The heptamethoxy flavone was twice crystallised from alcohol when it came

out in the form of colourless rectangular plates, melting at 129–31°. (Found: C, 61·2; H, 5·9; OCH_3, 50·4; $C_{22}H_{24}O_9$ requires C, 61·1; H, 5·6; OCH_3, 50·2%.)

6 : 8-*Dihydroxy-quercetin* (*X*).—

Product (B) (0·5 g.) was demethylated using hydriodic acid (10 c.c.) in acetic anhydride solution by boiling for half an hour at 140–50°. The cooled solution was then poured into water, and iodine removed with sulphur dioxide. The flavonol was obtained as a yellow crystalline (rectangular plates) powder. It was filtered, washed with water and dried. The crystallisation was effected using a large excess of dry ethyl acetate when the compound came out as yellow rectangular plates and flat needles. On heating it darkened in colour above 340° and exhibited no other change till 360°. The crystals turned orange-red on treatment with concentrated suphuric acid and then formed a yellow solution which did not exhibit any fluorescence in daylight. The alcoholic solution gave with ferric chloride an intense green colour which changed to brown. (Found: C, 53·7; H, 3·1; $C_{15}H_{10}O_9$ requires C, 53–9; H, 3·0%.) With 5% sodium bicarbonate it first gave a yellow solution which rapidly changed to greenish blue and deep blue within ½ minute and then faded to light green with a green precipitate; with 5% sodium carbonate the colours were yellow, emerald green, deep blue, fading and turning green, brownish yellow and finally brown; with 5% caustic alkali it immediately gave reddish brown changing to dark red.

The flavonol was acetylated by boiling with acetic anhydride and a drop of pyridine. The acetate was crystallised from acetone-ethyl alcohol mixture as previously described when it came out in the form of colourless rectangular plates and prisms melting at 221–22° with sintering at 219°. (Found: C, 55·6; H, 4·0; $C_{29}H_{24}O_{16}$ requires C, 55·4; H, 3·8%.)

5-*Hydroxy*-3 : 6 : 7 : 8 : 3′ : 4′ : 5′-*heptamethoxy-flavone* (*XI*).—

An intimate mixture of trimethyl gallic anhydride (5·0 g.), potassium trimethyl gallate (3·0 g.) and the ketone (V) (0·75 g.) was heated *in vacuo* at 175–80° for a period of 5 hours and the product worked up as before. There was no precipitate from the aqueous alkali solution that was first obtained, indicating absence of the fully methylated compound. However after saturation with carbon dioxide a yellow product separated out and it was extracted with ether. On removing the solvent, it came out as a viscous liquid which solidified on keeping in an ice-chest for 3 days. It crystallised from alcohol as bright yellow rectangular plates melting at 113–15°. It gave a brownish green colour with alcoholic ferric chloride and formed a

sparingly soluble potassium salt with alcoholic potash indicating the presence of a free hydroxyl in the 5-position. (Found: C, 59·2; H, 5·6; OCH_3, 48·6; $C_{22}H_{24}O_{10}$ requires C, 58·9; H, 5·4; OCH_3, 48·4%.)

3:5:6:7:8:3′:4′:5′-*Octamethoxy-flavone* (*XII*).—

The above methyl ether (XI) (0·2 g.) was further methylated in acetone solution using dimethyl sulphate and anhydrous potassium carbonate by boiling for 12 hours. The product was obtained as a liquid which solidified on keeping in the ice-chest for a number of days. It was crystallised from dilute alcohol when it came out as colourless rectangular plates melting at 122–23°. It did not give any colour with ferric chloride and did not dissolve in dilute alkali or impart any colour to the solution. (Found: C, 60·1; H, 5·7; OCH_3, 53·4; $C_{23}H_{26}O_{10}$ requires C, 60·0; H, 5·6; OCH_3, 53·7%.)

6:8-*Dihydroxy-myricetin* (*XIII*).—

The above 5-hydroxy-heptamethoxy-flavone (XI) (0·5 g.) was demethylated using hydriodic acid as already described. On pouring the cooled reaction mixture into ice-water and reducing iodine with sulphur dioxide, the flavonol separated out as a dark green solid. Direct crystallisation from dry ethyl acetate did not remove amorphous impurities completely. It was therefore dissolved in dry acetone and petroleum ether (b.p. 60°) added until some sticky impurity separated out and settled down; the clear solution was then decanted. On slow evaporation of the solvents, the flavonol separated out in a crystalline condition. Final purification was effected by crystallisation from dry ethyl acetate when it appeared as greenish yellow rectangular plates. The substance darkened in colour at 340° and did not melt below 360°. It gave a deep green colour changing to brown with alcoholic ferric chloride. It assumed a green colour rapidly on exposure to moisture. (Found: C, 51·2; H, 3·1; $C_{15}H_{10}O_{10}$ requires C, 51·4; H, 2·9%.) With 5% sodium bicarbonate, it gave immediately a blue solution turning deeper blue within 10 seconds; this rapidly faded to yellow with a green precipitate. With 5% sodium carbonate the colours were yellow, emerald green, blue, fading immediately to yellowish brown, red, yellowish brown and brown. With 5% caustic alkali it gave immediately a reddish brown solution changing to red.

The flavonol (XIII) (50 mg.) was acetylated using acetic anhydride and a drop of pyridine. The acetate was crystallised from acetone-ethyl alcohol mixture as already described when it came out as clusters of colourless rectangular plates melting at 225° with slight sintering at 221°. (Found: C, 54·2; H, 4·0; $C_{31}H_{26}O_{18}$ requires C, 54·2; H, 3·8%.)

Sodium amalgam in absolute alcohol.—

1. 6 : 8-*Dihydroxy-galangin.*—The solution turns green and then the colour gradually fades to greenish yellow with no flocks.

2. *Calycopteretin.*—The solution becomes green and changes to greenish yellow and then yellowish brown with no flocks.

3. 6 : 8-*Dihydroxy-quercetin.*—The solution turns green and immediately changes to brown and slowly precipitates brown flocks, while the solution becomes colourless.

4. 6 : 8-*Dihydroxy-myricetin.*—Brown solution, rapidly precipitates brown-pinkflocks, the solution becoming colourless.

Gossypetone reaction.—

1. 6 : 8-*Dihydroxy-galangin.*—The solution immediately becomes blue and rapidly changes to red; this fades on shaking to give a yellow solution changing finally to brown. After 24 hours it is coloured brown.

2. *Calycopteretin.*—The blue solution formed immediately changes to deep red and then to green, greenish yellow, brown and yellow. After 24 hours, it is yellow.

3. 6 : 8-*Dihydroxy-quercetin.*—The blue solution immediately changes to brown red and fades to pale yellow. Pale yellow after 24 hours.

4. 6 : 8-*Dihydroxy-myricetin.*—The alcoholic solution which was originally green changes to blue and turns into a stable intense red. It fades to brown during 24 hours.

Colour reactions with alkaline buffer solutions.—

1. 6 : 8-*Dihydroxy-galangin.—*

pH 8·0 Substance sparingly soluble, pale yellow solution changing to dirty green, blue, and deep violet blue fading within three minutes and becoming pale blue within six minutes. The pale blue slowly changes and becomes pale yellow within 24 hours.

pH 8·6 Substance difficultly soluble, pale yellow solution changing to blue and then to violet blue and fading within two minutes. The pale blue slowly fades and finally after 24 hours it becomes pale yellow.

pH 9·2 Substance more easily soluble than before; yellow solution changes to blue and fades faster within the first minute and

becomes yellow by four minutes. After 24 hours it becomes pale yellow.

pH 9·8 Substance dissolves quicker to a yellow solution and becomes blue, starts fading within 20 seconds and becomes pale blue in two minutes and yellow in four minutes. After 24 hours it becomes pale yellow.

pH 10·4 Pale yellow solution, changes very fast to blue and becomes pale yellow whithin 15 seconds. After 24 hours there is no change.

pH 11·0 Yellow solution quickly becoming yellowish green, pale blue and finally yellow. After 24 hours it is pale yellow.

pH 11·6 Yellow solution changing fast to yellowish green and greenish blue, becomes yellow within 30 seconds and then golden yellow. Slowly it fades to pale yellow within 24 hours.

pH 12·2 Same as above.

pH 12·8 Same as above.

pH 13·4 Same as above.

In general, the flavonol does not dissolve in the buffer solutions of lower pH readily. On boiling with distilled water, the substance forms a green solution which rapidly turns blue. With tap water the solution turns deeper blue than with distilled water and slowly fades and after 24 hours becomes pale yellow.

Calycopteretin.—

pH 8·0 Yellow solution, quickly changes to dirty green and to deep blue within half minute, more intense blue within one minute and starts fading within 3 minutes to bluish green. This slowly fades within 10 minutes to yellowish green and becomes pale yellow within 18 minutes. After 24 hours the solution becomes pale yellow.

pH 8·6 Yellow solution slowly changing to yellowish green, and blue in 20 seconds; starts fading after one minute and becomes greenish yellow within 8 minutes. After 24 hours it is pale yellow.

pH 9·2 The initial yellow solution quickly changes to green, blue and intense blue within half minute and fades rapidly to yellow in two minutes. Within six minutes the yellow intensifies and becomes golden yellow. After 24 hours it is pale yellow.

pH 9·8 Colour changes are very rapid; yellow solution turns quickly deep green and within half minute greenish yellow, becomes golden yellow within one minute and orange yellow within two minutes. The solution assumes a yellow colour after 24 hours.

pH 10·4 Yellow solution rapidly changes to green, and emerald green and becomes yellowish green within half minute and orange yellow within 45 seconds. The colour fades and becomes golden yellow after 24 hours.

pH 11·0 Same as above.

pH 11·6 Yellow solution; colour changes same as above and faster.

pH 12·2 Same as above. Changes faster than before giving orange yellow within 20 seconds and deeper yellow after 24 hours.

pH 12·8 Same as above.

pH 13·4 Yellow solution becomes greenish yellow and then fades to orange yellow. After 24 hours it becomes a deep yellow solution.

With distilled water, the substance becomes green changing to greenish blue. The solution is also of the same colour and changes to pure blue on boiling.

6 : 8-*Dihydroxy-quercetin.*—

pH 8·0 Yellow solution becoming deep yellow; turns rapidly yellowish green, green, and emerald green and within 30 seconds turns blue and intensifies to deeper blue in 6 minutes. The blue fades slowly and turns to deep yellow in 24 hours.

pH 8·6 Yellow solution going into deep green within 20 seconds; becomes blue within ½ minute and intensifies to deep blue within one minute and fades after 3 minutes. Becomes pale yellow in 24 hours.

pH 9·2 Yellow solution, quickly changes to green and blue within 20 seconds, starts fading within 2 minutes and becomes yellowish green after 6 minutes and yellow after 10 minutes, and pale orange after ½ an hour. Pale yellow solution after 24 hours.

pH 9·8 Yellow solution, changes very fast to greenish yellow and then blue, fades within 30 seconds and becomes greenish

yellow within one minute and yellow in 3 minutes. In 10 minutes becomes orange yellow which fades slowly and becomes yellow in 24 hours.

pH 10·4 Very fast changes; yellow solution immediately turns green and emerald green and becomes greenish yellow and yellow within 20 seconds. It assumes a golden yellow colour within one minute and orange within 2 minutes; subsequently fades to paler orange within half an hour; yellow in 24 hours.

pH 11·0 Same as above; within one minute deeper orange than above and fades within half an hour to pale orange; solution deep yellow after 24 hours.

pH 11·6 Same as above; assumes orange with ½ minute and orange red within one minute; fades after 30 minutes and becomes deep yellow in 24 hours.

pH 12·2 Same as above; deep orange red within 45 seconds and starts fading to become deeper yellow in 24 hours.

pH 12·8 Same as above; within 30 seconds deeper orange red; fades after one hour to give deep yellow in 24 hours.

pH 13·4 Same as above. Solution deeper yellow after 24 hours.

Substance treated with distilled water gives a blue colour in the cold; the colour of the solution changes to green after boiling, fades after ½ hour and becomes pale yellow after 24 hours.

6:8-*Dihydroxy-myricetin.*—

pH 8·0 Yellow solution changes to yellowish green, green and emerald green and becomes deep blue within one minute; after 10 minutes becomes emerald green and fades after one hour. Deep yellowish brown after 24 hours.

pH 8·6 Yellow solution changes to greenish yellow and then rapidly to green and blue within ½ minute. Fades after 3 minutes to green and becomes pale yellowish green after 6 minutes; in one hour becomes pale yellow; yellow in 24 hours.

pH 9·2 Yellow solution, changing fast to green and then blue within 20 seconds; starts fading after 1½ minutes; yellowish green within 4 minutes and pale yellow in 24 hours.

pH 9·8 Yellow solution rapidly changing to green and emerald green; fades to green within 20 seconds and yellowish green in 2 minutes; brownish yellow in 24 hours.

pH 10·4 Yellow solution changing to green and emerald green and fading to yellowish brown within 40 seconds; colour turns brown within one minute, changes to brown red and reddish purple and fades to reddish brown after 2 minutes, becomes brown within 5 minutes and orange brown within 10 minutes. After 24 hours it is orange red.

pH 11·0 Yellow solution changing fast to yellowish green and to reddish purple within one minute and then brilliant purple; slowly fades to reddish brown in 12 minutes and orange red in 24 hours.

pH 11·6 Very rapid changes; initial yellow solution changes to yellowish green, yellowish brown and brown purple within 20 seconds and then to bluish purple; fades after one minute rapidly to reddish brown and becomes yellowish brown after 4 minutes; after 24 hours orange red.

pH 12·2 Faster changes, same as above.

pH 12·8 Yellow solution changing fast to green, emerald green and yellowish brown within 20 seconds, becomes brown and brown purple and bluish purple and fades to reddish brown in one minute and pale brown in 6 minutes; after 24 hours orange red.

pH 13·4 Same as above.

On treatment with distilled water the substance turns blue in the cold. The solution becomes deeper blue on warming and fades to pale green after 1½ hours. It is greenish yellow after 24 hours.

Our thanks are due to Mr. A. N. Ratnagiriswaran for the gift of several grams of calycopterin.

Summary

The constitution of calycopteretin has been confirmed by the decomposition of the fully methylated ether with alcoholic alkali and also by its synthesis from the decomposition products. Alkaline hydrolysis of the fully methylated ether yields anisic acid and 2-hydroxy-ω-3 : 4 : 5 : 6-pentamethoxyacetophenone. Condensation of this ketone with sodium anisate and anisic anhydride, regenerates calycopterin dimethyl ether. When the anhydride

and sodium salt of benzoic acid are used instead, 3:5:6:7: 8-pentamethoxy flavone is readily formed. On demethylation, it yields 6:8-dihydroxy-galangin. When, however, the sodium salt and anhydride of veratric acid are used, partial demethylation takes place in the 5-position, giving rise to both hexamethyl and heptamethyl ethers. By complete demethylation, 6:8-dihydroxy-quercetin is obtained. Using gallic acid derivatives for the condensation, demethylation is found to be complete in the 5-position yielding 5-hydroxy-heptamethoxy-flavone. Methylation of this produces the octamethyl ether and demethylation the octahydroxy compound, 6:8-dihydroxy-myricetin. This is the most highly hydroxylated of flavones known so far.

A comparative study of the properties of the four flavonols of this group, their methyl ethers and acetates has been made. Colour reactions useful for rapid identification are also described. They are remarkable in several respects.

The properties of mono-methyl erianthin do not agree with those of 5-hydroxyhexamethoxy-flavone prepared in the course of this work.

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CONSTITUTION OF CALYCOPTERIN

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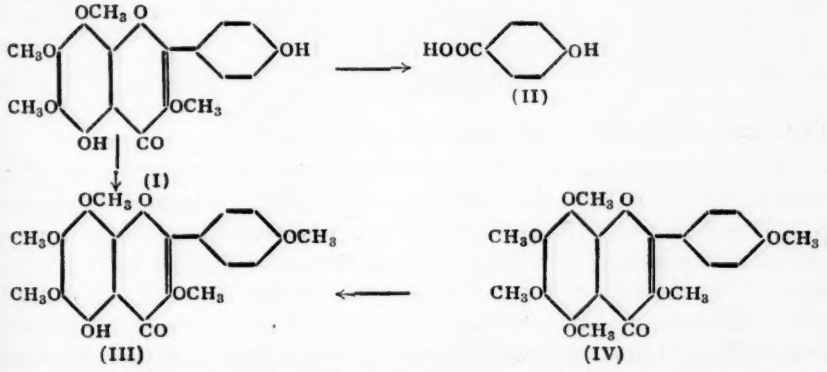
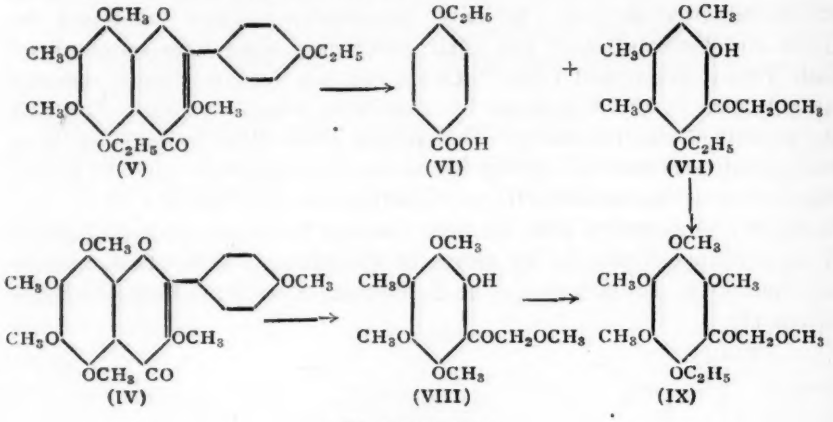
Calycopterin is a tetramethyl ether of calycopteretin which is 3:5:6:7:8:4′-hexahydroxy-flavone. Its exact constitution was first investigated by Gulati and Venkataraman[1] and their conclusions were later modified by Shah, Venkataraman and Virkar.[2] Of the two free hydroxyl groups, one was easily located in the 4′-position by identifying *p*-hydroxybenzoic acid (II) as a product of alkaline fission. The position of the other hydroxyl has been finally fixed as 5, since this group is resistant to methylation and the monomethyl ether of calycopterin (III) gives reactions characteristic of a 5-hydroxyl. Further this monomethyl ether has been obtained by the partial demethylation of the dimethyl ether (IV) by means of hydrobromic acid. Consequently calycopterin is considered to be 5:4′-dihydroxy-3:6:7:8-tetramethoxy-flavone (I).



The above constitution has now been confirmed in a different way. Calycopterin is ethylated by means of ethyl iodide and potassium carbonate in acetone solution and the diethyl ether (V) obtained in good yield. When subjected to fission with alcoholic potash, it yields an acid product which is identified as *p*-ethoxybenzoic acid (VI) locating an ethoxyl in the 4′-position of the flavone. The other part is a ketone having the composition and the characteristic properties of 2-hydroxy-monoethoxy-tetramethoxy-acetophenone (VII). In order to determine its constitution it is further methylated by means of dimethyl sulphate and anhydrous potassium carbonate

in acetone solution. This product is found to be identical with the ethylation product (IX) of 2-hydroxy-ω: 3: 4: 5: 6-pentamethoxyacetophenone (VIII). The identity has been established not only by direct comparison but also by the preparation of derivatives. This is possible only if in calycopterin, a free hydroxyl exists in the 5-position which is substituted by an ethoxyl in the ethyl ether. The various transformations described above are diagrammatically represented below:



EXPERIMENTAL

Ethylation of calycopterin:—Diethyl-calycopterin (V).—

Calycopterin (1 g.) dissolved in acetone (20 c.c.) was boiled under reflux with excess of ethyl iodide (3·0 c.c.) and anhydrous potassium carbonate (10 g.) for a period of 15 hours. The solution which was originally orange red became practically colourless towards the end. The solvent was then removed by distillation, and the residue treated with ice-water. The ethyl ether which separated out as a liquid solidified during the course of half an hour. When it was crystallised from alcohol it came out as colourless rhombohedral prisms melting at 131–32° (Karrer[3], mp. 130°). It was insoluble in dilute alkali and did not give any colour with alcoholic ferric chloride. The mixed melting point with dimethyl-calycopterin was depressed, 105–115°. (Found: C, 64·1; H, 6·1; $C_{23}H_{26}O_8$ requires C, 64·0; H, 6·0%.) It was easily soluble in acetone, ethyl acetate and hot alcohol and very sparingly soluble in cold alcohol.

Decomposition of diethyl calycopterin with alcoholic potash.—

Diethyl-calycopetrin (1·0 g.) was boiled under reflux with absolute alcoholic potash (30 c.c., 8%) for a period of six hours. At the end of the

operation, as much of the alcohol as possible was removed by distillation and the residue dissolved in water. The solution was then filtered from any suspended insoluble impurities and the clear filtrate was acidified with dilute sulphuric acid. It was then ether-extracted several times and the combined ether extract was shaken three times with 5% sodium bicarbonate solution to remove the acid part (A).

The ketonic part.—The ether solution was then washed with water and on distilling off ether it gave a pale yellow liquid which solidified during the course of a few hours. It was purified by crystallisation from light petroleum (B.P. 60°) when it came out in the form of pale yellow thin rectangular plates melting at 75–77° (Karrer[3] gives mp. 63–64°). It dissolved in alkali to give a yellow solution and gave an olive-green colour with alcoholic ferric chloride. It is highly soluble in water even in the cold. (Found: C, 55·9; H, 6·6; $C_{14}H_{20}O_7$ requires C, 56·0; H, 6·7%.)

The acid part.—The bicarbonate solution (A) on acidification with concentrated hydrochloric acid precipitated a crystalline material which was ether extracted. The residue obtained after removal of ether was purified by crystallisation from hot water or 10% alcohol when it came out in the form of colourless shining needles melting at 197–98°. The mixed melting point with a synthetic sample of *p*-ethoxy-benzoic acid (see below) was undepressed. (Found: C, 65·2; H, 6·2; OC_2H_5, 26·9; $C_9H_{10}O_3$ requires C, 65·1; H, 6·0; OC_2H_5, 27·1%).

p-Hydroxy-benzoic acid (1·0 g.) was ethylated in acetone solution with ethyl iodide (3·0 c.c.) and anhydrous potassium carbonate by boiling for a period of 15 hours. The solvent was removed by distillation and the residue treated with water. The ether-ester that separated out as a liquid was twice extracted with ether. On removing the solvent it was again obtained as a liquid. It was then hydrolysed by boliing with 20% sodium hydroxide solution (20 c.c.) for half an hour and the acid obtained on acidification, was crystallised from 10% alcohol when it came out as colourless shining needles melting at 197–98°. Yield 0·9 g.

The aqueous potassium carbonate solution from which the ether had separated was acidified with dilute sulphuric acid when a crystalline precipitate separated out. It was crystallised from 10% alcohol and was found to be *p*-ethoxy-benzoic acid. Yield 0·1 g. Thus in the process of ethylation of *p*-hydroxy-benzoic acid some acid is formed along with the ester.

ω: 2: 3: 4: 5-*pentamethoxy*-6-*ethoxy-acetophenone* (*IX*).—

The above ketone was methylated in acetone solution by boiling with dimethyl sulphate and anhydrous potassium carbonate for a period of ten

hours. The solvent was then removed by distillation, and the residue treated with water when an insoluble liquid separated out and it was extracted with ether. Removal of the solvent gave the methyl ether as a viscous liquid. It did not solidify on keeping in the ice-chest for a number of days and attempts at crystallisation were not successful. It was insoluble in aqueous alkali and did not give any colour with alcoholic ferric chloride. Hence it was considered to be the required ketone and was further identified as its 2:4-dinitrophenyl-hydrazone. This was prepared by boiling the ketone with an alcoholic solution of denitro-phenyl-hydrazine and was obtained as deep red rhombohedral prisms by crystallisation from alcohol or acetic acid melting at 198–99°. (Found: C, 57·7; H, 5·9; $C_{21}H_{26}O_{10}N_4$ requires C, 57·5; H, 5·9%.) A mixed melting point with 2:4-dinitro-phenyl-hydrazine was depressed.

Ethylation of 2-hydroxy-ω:3:4:5:6-pentamethoxy-acetophenone (VIII).—

ω:2:3:4:5-pentamethoxy-6-ethoxy-acetophenone (IX).—

2-Hydroxy-ω:3:4:5:6-pentamethoxy-acetophenone[4] was ethylated in acetone solution by boiling with ethyl iodide and potassium carbonate. The product on working up came as a liquid which could not be solidified. It was insoluble in dilute aqueous alkali and did not give any colour with alcoholic ferric chloride. It was identified as its 2:4-dinitrophenylhydrazone. This was prepared as before and it crystallised from acetic acid as deep red rhombohedral prisms melting at 198–99°. A mixed melting point with the sample obtained previously was undepressed.

Summary

The constitution of calycopterin as 5:4′-dihydroxy-3:6:7:8-tetramethoxy-flavone has been confirmed. Calycopterin diethyl ether has been shown to have ethoxyl groups in the 5 and 4′-positions, since on fission with alcoholic alkali, it yields *p*-ethoxy benzoic acid and 2-hydroxy-ω:3:4:5-tetramethoxy-6-ethoxy acetophenone. The constitution of the ketone has been established by methylation and comparison with a synthetic sample obtained by the ethylation of ω:2:3:4:5-pentamethoxy-6-hydroxy-acetophenone.

References

1. Gulati and Venkataraman .. *J. C. S.*, 1936, 267.
2. Shah, Virkar and Venkataraman .. *J. I. C. S.*, 1942, **19**, 135.
3. Karrer, W. .. *Helv.*, 1934, **17**, 1560.
4. Seshadri and Venkateswarlu .. *Proc. Ind. Acad. Sci.*, A 1946, **23**, see previous paper.

A NOTE ON THE CONSTITUTION OF ALPINETIN

BY K. VISWESWARA RAO AND T. R. SESHADRI

(From the Department of Chemistry, Andhra University)

Received March 5, 1946

FROM the ether extract of the seeds of *Alpinea chinesis*, Kimura[1] isolated alpinetin having a melting point of 223°. Based on a study of its properties and reactions, he considered it to be 5-hydroxy-7-methoxy-flavanone. A substance of this constitution had already been prepared synthetically by Shinoda and Sato[2] and its melting point recorded as 101°. They made it by the partial methylation of 5:7-dihydroxy-flavanone using diazomethane. In view of this discrepancy, 5-hydroxy-7-methoxy flavanone has now been prepared in a different way by the partial demethylation of 5 : 7-dimethoxy flavanone using aluminium chloride in nitrobenzene solution. In its properties it agrees with the description of Shinoda and Sato and it melts at 101–02°. Alpinetin cannot, therefore, be identical with this flavanone and its constitution should be considered as unsettled.

EXPERIMENTAL

5:7-Dimethoxy-flavanone.—

4:6-Dimethoxy-2-hydroxy-acetophenone required for the present purpose was prepared by the partial methylation of phloracetophenone as described by Sastri and Seshadri.[3] It melted at 88–89° and gave a reddish brown colour with ferric chloride.

In the conversion of this ketone into 4:6-dimethoxy-2-hydroxy-chalkone[4] the yields and the quality of the product could be improved by adopting the following procedure.

A mixture of 4:6 dimethoxy-2-hydroxy-acetophenone (3 g.) and benzaldehyde (9 c.c.) was dissolved in alcohol (20 c.c.) and treated with a strong solution of potash (25 g. of potash in 20 c.c. of water) while cooling in ice. Enough alcohol was then added to get a homogeneous solution and the flask tightly stoppered and left for 3 days at the room temperature. The contents were then diluted with water, extracted twice with ether (A) and the clear alkaline layer acidified with concentrated hydrochloric acid. The product was extracted with ether and the ether solution washed well with aqueous sodium bicarbonate. On distilling off the ether the chalkone was obtained as a red liquid which soon solidified. Yield, 4·0 g.; m.p. 90–91°.

When the ether extract (A) was evaporated, it left a reddish brown oily residue. It was treated with excess of petroleum ether and the mixture kept in the ice-chest. A pale yellow crystalline solid separated out. It was filtered, washed with small quantities of ether and crystallised from a mixture

of benzene and petroleum ether from which it separated in the form of colourless rectangular plates and prisms melting at 143–44°. It was identical with the flavanone described below (Kostanecki and Tambor recorded the melting point of 5: 7-dimethoxy flavanone as 1.

For the conversion of the chalkone into the flavanone the former was refluxed with aqueous alcoholic sulphuric acid for 24 hours. The product was ground well with aqueous alkali to remove unchanged chalkone, washed with a little ether to remove coloured impurities and finally crystallised from benzene-petroleum ether mixture. The flavanone separated out as colourless rectangular plates and prisms melting at 143–44°. It was insoluble in aqueous alkali and did not give any colour with ferric chloride. In concentrated nitric acid it dissolved to produce an intense blue colour. When reduced with magnesium and hydrochloric acid in an alcoholic solution, it gave an orange yellow colour.

5-Hydroxy-7-methoxy-flavanone.—

A solution of 5: 7-dimethoxy-flavanone (0·5 g.) in dry nitrobenzene was treated with a solution of anhydrous aluminium chloride (1 g.) in the same solvent. After keeping the solution at 100° for 1 hour, it was cooled and treated with excess of petroleum ether, whereby most of the nitrobenzene was dissolved, leaving behind a greenish semi-solid mass. It was washed twice with petroleum ether and finally decomposed with dilute hydrochloric acid. The solution along with the solid product was extracted with ether and the ether solution repeatedly shaken with dilute sodium hydroxide solution. A bulky precipitate separated at this stage in the aqueous medium but this dissolved on adding more of water. The alkaline solution was filtered and acidified with hydrochloric acid. The precipitated solid was filtered, washed with water and crystallised successively from alcohol and a mixture of benzene and petroleum ether. 5-Hydroxy-7-methoxy-flavanone crystallised in the form of stout prismatic needles melting at 101–02°. (Found: C, 71·1; H, 5·4; CH_3O, 11·0; $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2 and CH_3O, 11·5%.)

It was sparingly soluble in cold aqueous alkali. In alcoholic solution it gave a deep brown colouration with ferric chloride and an orange colour with magnesium and hydrochloric acid. In concentrated nitric acid it dissolved to a fine blue solution.

References

1. Kimura ... *Chemical Abstracts*, 1940, 4063.
2. Shinoda and Sato ... *Ibid.*, 1929, 837.
3. Sastri and Seshadri ... *Proc. Ind. Acad. Sci.*, A, 1946, **23** (see next issue of the *Proceedings*).
4. Kostanecki and Tambor ... *Ber.*, 1899, 2260.

ARYL ESTERS AND ARYLAMIDES OF 2-HYDROXY-3-NAPHTHOIC ACID AND 1-BROMO-2-HYDROXY-3-NAPHTHOIC ACID

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(Communicated by Prof. R. C. Shah, F.A.SC.)

The aryl esters of the acids are prepared by heating the respective phenol and the acid in presence of phosphorus oxy-chloride at 130–140° C. The esters of the bromo acid and *o*-anisidide and *o*-toluidide of the bromo acid are also obtained by the bromination of the esters and the corresponding arylamides of the simple hydroxy acid.

The method for the preparation of arylamides of 2-hydroxy-3-naphthoic acid are either covered by patents or are very tedious,[1] probably because the preparation of its acid chloride is very tedious.[2] Now it is found that these arylamides can be easily prepared by heating the mixture of the acid and the amine with excess of phosphorus trichloride.

In the case of 1-bromo-2-hydroxy-3-naphthoic acid, however, as the acid chloride can be easily prepared by the action of phosphorus pentachloride on the acid in presence of dry benzene, its arylamides are prepared by the interaction of the acid chloride and the respective amine in presence of dry benzene at room temperature.

Experimental

Preparation of aryl esters.—

The acid and the phenol were taken in equal weights and phosphorus oxychloride whose volume was equal to half the weight of the acid was added to the mixture. The mixture was heated at 130–40°, until a clear solution was obtained. When cold, the reaction mixture was diluted with water and separated solid was washed completely. All the substances are crystallised from acetic acid. They are described in Table I.

2-Hydroxy-3-naphth-o-toluidide.—A mixture of the acid (4 g.) and freshly distilled *o*-toluidine (5 g.) was heated to melt the acid and then phosphorus trichloride (10 c.c.) was added through the top of the condenser and the mixture was heated at 160–70° for two hours. When cold, the mixture was titurated with dilute hydrochloric acid and washed with water. It

TABLE I

Substance	Crystalline shape	M.P.	Formula	Found	Required	Yield %
o-Cresyl-2 hydroxy-3-naphthoate	Yellow needles	119–20°	$C_{18}H_{14}O_3$	C, 77·4; H 5·0;	C, 77·7 H, 5·0	85
m-Cresyl-2-hydroxy-3-naphthoate	Pale yellow needles	94–5°	$C_{18}H_{14}O_3$	C, 77·7; H, 4·4;	C, 77·7 H, 5·0	80
*Phenyl-1-bromo-2-hydroxy-3-naphthoate	Pale yellow needles	131–2°	$C_{17}H_{11}O_3$ Br.	Br, 23·0;	Br, 23·3	75
**o*-Cresyl-1-bromo-2-hydroxy-3-naphthoate	Yellow needles	163–4°	$C_{18}H_{13}O_3$ Br.	Br, 22·4;	Br, 22·4	75
**m*-Cresyl 1-bromo-2-hydroxy-3-naphthoate	Pale yellow needles	146–7°	$C_{18}H_{13}O_3$ Br.	Br, 22·7;	Br, 22·4	75

crystallised from acetic acid in small white needles, m.p. 192–3°. Yield 35%. (D.R.P. 293,897 gave m.p. 195–6°). (Found: N, 4·8; $C_{18}H_{15}O_2N$ requires N, 5·1 per cent.)

2-*Hydroxy*-3-*napth-m-toluidide.*—A mixture of the acid (5 g.), *m*-toluidine (6 g.) and phosphorus trichloride (20 c.c.) was heated under reflux at 170–80° for two hours and then worked up as above. It crystallised from acetic acid in shining plates, m.p. 213–14°. Yield 80%. Found: N, 4·9; $C_{15}H_{15}O_2N$ requires N, 5·1 per cent.)

2-*Hydroxy*-3-*naphth*-o-*anisidide.*—A mixture of the acid (5 g.), *o*-anisidine (7 g.) and phosphorus trichloride (20 c.c.) was heated under reflux at 170-90° for two and a half hours and then worked up as before. It crystallised from acetic acid in small needles, m.p. 162–4°. Yield 20%. (D.R.P. 293, 897 gave m.p. 167–8°.) (Found: N, 4·5; $C_{18}H_{15}O_3N$ requires N, 4·8 per cent.)

1-*Bromo*-2-*hydroxy*-3-*naphthoyl chloride.*—A mixture of the acid (3 g.) and phosphorus pentachloride (3 g.) and dry benzene (10 c.c.) was heated gently on a water-bath until a clear orange solution was obtained. On cooling the solution, yellow needles of the acid chloride separated out. The solid was washed with dry petroleum ether and dried in vacuum over phosphorus pentoxide, m.p. 145–6°. (Found: Cl, 12·2; ; Br, 27·6; $C_{11}H_6O_2ClBr$ requires Cl, 12·4; Br, 28·0 per cent.)

Arylamides of 1-*bromo*-2-*hydroxy*-3-*naphthoic acid.*—The acid chloride prepared from a certain weight of the acid was dissolved in sufficient quantity of dry benzene (10 times in vol. of the weight taken) and to it the amine, whose volume was equal to the weight of the acid taken, dissolved in a little dry benzene was added and the mixture was left at room temperature for one hour. The solid obtained after the removal of the solvent was treated with dilute hydrochloric acid, washed with water and then crystallised from acetic acid. The substances are described in Table II.

TABLE II

Substance	Crystalline shape	M.P.	Formula	Found	Required	Yield %
1-Bromo-2-hydroxy 3-naphthanilide	Pale yellow needles	165–6°	$C_{17}H_{12}O_2NBr$	Br, 23·1	Br, 23·4	60
*1-Bromo-2-hydroxy-3-naphtha-*o*-toluidide	Yellow needles	234–5°	$C_{18}H_{14}O_2NBr$	Br, 22·3	Br, 22·5	56
1-Bromo-2-hydroxy-3-naphth-*m*-toluidide	Yellow plates	171–2°	$C_{18}H_{14}O_2NBr$	Br, 22·9	Br, 22·5	75
1-Bromo-2-hydroxy-3-naphth-*p*-toluidide	Pale yellow needles	201–2°	$C_{18}H_{14}O_2NBr$	Br, 22·6	Br, 22·5	70
*1-Bromo-2-hydroxy-3-naphth-*o*-anisidide	Yellow needles	191–2°	$C_{18}H_{14}O_3NBr$	Br, 21·9	Br, 21·5	60
1-Bromo-2-hydroxy 3-naphth-*p*-anisidide	Yellow plates	173–4°	$C_{18}H_{14}O_2NBr$	Br, 21·2	Br, 21·5	60

Substances marked * are prepared by direct condensation as well as by the bromination of the corresponding derivatives of the 2 hydroxy-3 napthoic acid.

(The preparation of *o*- and *m*-cryesyl esters of 2-hydroxy-3-napthoic acid and *o*- and *m*-toluidides and *o*-anisidide of the same acid as well as phenyl, *o*- and *m*-cresyl esters and anilide, *o*-, *m*- and *p*-toluidides and *o*- and *p*-anisidides of 1-bromo-2-hydroxy-3-naphthoic acid is described. The esters and *o*-toluidide and *o*-anisidide of 1-bromo-2-hydroxy-3-naphthoic acid are also prepared by the bromination of the corresponding derivatives of the 2-hydroxy-3-naphthoic acid.)

Bromination of the phenyl, o-, *and* m-*cresyl esters and* o-*toluidide and* o-*anisidide of 2-hydroxy-3-naphthoic acid.*—

The requisite ester (2 g.) was mixed with dry chloroform (10 c.c.) and the solution of bromine in the same solvent (14 c.c. of 10% solution) was gradually added to it. The reaction mixture was left at room temperature for half an hour and then the solvent was removed. The bromo-derivative was crystallised from acetic acid and mixed melting point with the authentic specimen described in Table I was taken, when no lowering in melting point was observed.

In the bromination of *o*-toluidide and *o*-anisidide the same method was used, but they being less soluble, more solvent was used, the proportion of the reactants being 1 : 1. These products also were crystallised from acetic acid and mixed melting points with authentic specimens described in Table II showed no lowering.

REFERENCES

1. Schoff .. *Ber.*, 1892, **25**, 2743; Brit. patent 289037; U. S. patent 1,733, 468 of 1937; Jap. patent 95038 of 1932; D. R. P. 289027, 293897, 294799 of 1916.
2. Meyer .. M. 1901, **22**, 791.
   Fries .. *Ber.*, 1925, **58**, 2848; French patent 632,767 (1927); U. S. patent 1,684,273 (1927); *J. Gen. Chem.* (U. S. S. R.), 1938, **8**, 557–64.

STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XXVII. The Rotatory Dispersion of Stereoisomeric 2 : 5-Dichloroanilino-, 3-Nitro-4-chloroanilino , 2-Nitro *p*-toluidino- and 4-Nitro-*o* toluidino methylenecamphors

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Received February 22, 1946

IN continuation of our studies, Part XXIV in this series,[1] we have now investigated the rotatory dispersion of the condensation products of oxymethylenecamphors (*d*, *l*, *dl*) and 2:5-dichloroaniline, 3-nitro-4-chloroaniline, 2-nitro-*p*-toluidine and 4-nitro-*o*-toluidine.

INFLUENCE OF CHEMICAL CONSTITUTION ON ROTATORY DISPERSION

Rotatory dispersions may be classified as "Simple" or "Complex" according as they can, or cannot, be expressed by Drude's one-term equation, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$. The condensation products of oxymethylenecamphors and aromatic amines, described here, were found to obey the simple dispersion formula exactly. On plotting $\frac{1}{[\alpha]}$ against λ^2, exact straight lines were obtained (Fig. 1).

Out of 430 observations recorded in this paper (Tables III–VI), in as many as 398 cases the difference (*o–c*) between the observed (*o*) and the calculated (*c*) values of specific rotation corresponds to a difference of 0·02° or less in the corresponding angles of rotation. In 22 cases this difference lies between 0·02° and 0·03°, and only in 10 cases, most of which are for Hg_{4358} (Mercury violet)—a difficult line to read—this difference lies between 0·03° and 0·05°. All these differences (*o–c*), not given here for economy of space, are, however, of the nature of casual experimental errors.

PHYSICAL IDENTITY OF ENANTIOMERS

Pasteur's Law of Molecular Dissymmetry, according to which the *d*- and *l*-forms of a substance possess identical physical properties as regards their magnitude has been found to hold good: the values of the rotatory power of the *d*- and *l*-forms of the compounds in different solvents (Tables III–VI) are identical within the limits of experimental error.

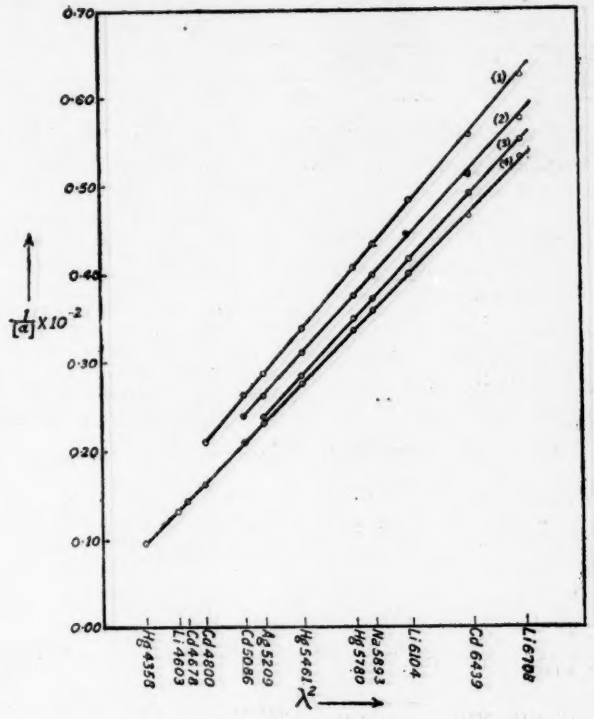


FIG. 1

(1) 2-Nitro-*p*-toluidinomethyl ene-*d*-camphor in benzene.
(2) 3-Nitro-4-chloroanilinomethyl ene-*d*-camphor in chloroform.
(3) 4-Nitro-*o*-toluidinomethyl ene-*d*-camphor in methyl alcohol.
(4) 2 : 5-Dichloroanilinomethyl ene-*d*-camphor in methyl alcohol.

EFFECT OF THE NATURE OF THE SUBSTITUENT GROUP ON THE ROTATORY POWER

The polar effect of substituent group is traceable in optical activity.[1,2]

In the present investigation we have studied the effect on rotation of three substituents, Cl, CH_3 and NO_2 groups, which are assigned polarities in accordance with the following polar series[3] deduced from specific inductive capacities: $\overline{OH}$, Cl, Br, I, C_2H_5, $\overline{CH_3}$, $\overset{+}{H}$, CO_2H, CHO, $COCH_3$, CN, $\overset{+}{NO_2}$. From this study it is found that the effect of substituents on the rotatory power can be generally correlated with their polarities as is evident from the following account:—

(1) Cl, on account of its negative polarity, lowers the rotatory power of the parent compound as supported by the following observations (Table I):

TABLE I

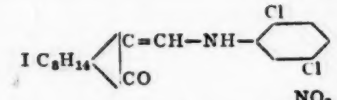
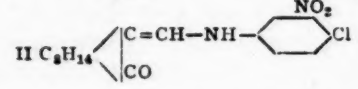
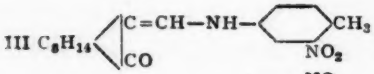
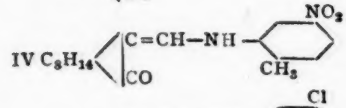
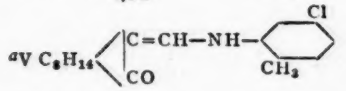
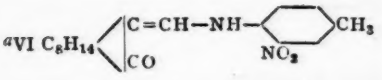
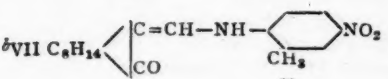
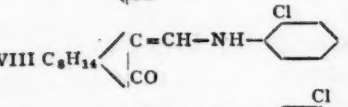
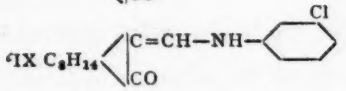
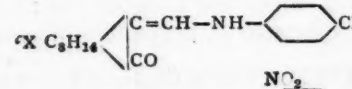
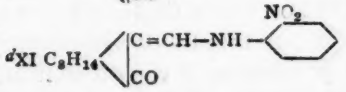
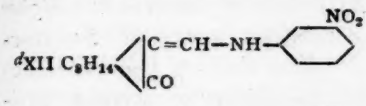
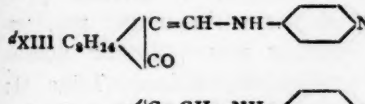
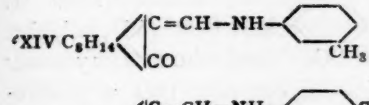
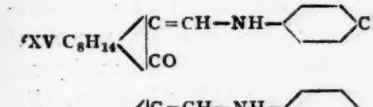
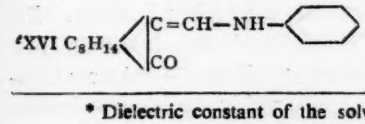
Structural formulæ	$[\alpha]^{35°\ C.}_{Hg_{5461}}$					
	MeOH 31·2°	EtOH 25·8°	Acetone 21·5°	Pyridine 12·4°	Chloroform 5·2°	Benzene 2·28°
 I C_8H_{14}	360·0° (60·17)	351·0° (57·76)	352·0° (58·11)	358·0° (59·45)	356·0° (57·76)	344·0° (56·94)
 II C_8H_{14}	380·0 (65·59)	365·0 (65·32)	360·0 (64·45	350·0 (61·69)	320·0 (57·11)	290·0 54·14)
 III C_8H_{14}	388·0 (66·68)	376·0 (66·21)	368·0 (65·54)	362·0 (6··2)	330·0 61·26	295·0 (52·39)
 IV C_8H_{14}	350·0 (57·16)	352·0 (57·8)	355·0 (58·58)	370·0 (58·03)	353·0 (56·38	339·0 (55·24)
 [a]V C_8H_{14}	386·0 (62·6)	378·0 (60·7)	380·0 (62·5)	390·0 (63·6)	373·0 (60·4)	361·0 (58·5)
 [a]VI C_8H_{14}	492·9† (65·46)	459·5† (62·44)	464·1† 60·26)	416·4† (57·32)	458·5† (64·16)	390·0 (59·45)
 [b]VII C_8H_{14}	491·8 (70·4)	500·7 (67·43)	522·1 (70·01)	561·5 (70·2)	523·3 (66·63	479·4 (66·71)
 [c]VIII C_8H_{14}	400·2 (64·77)	405·8 (72·23)	380·0 (61·42)	391·3 (63·72)	386·0 (61·79)	364·7 (57·76)
 [c]IX C_8H_{14}	388·5 63·14	384·7 (62·47)	388·0 (63·65	374·4 (63·70)	381·4 (61·22)	363·6 60·73)
 [c]X C_8H_{14}	417·7 (75·34)	406·3 (73·20)	401·8 (70·58)	394·4 (68·19)	374·6 (67·56)	359·4 (57·80)
 [d]XI C_8H_{14}	493·1† (57·80)	.. ..	468·1† (59·07)	424·8† (72·06)	484·† (45·54	399·2 (50·26)

TABLE I—(*Contd.*)

Structural formulæ	$[\alpha]^{35°\,C.}_{Hg_{5461}}$					
	MeOH 31·2*	EtOH 25·8*	Acetone 21·5*	Pyridine 12·4*	Chloroform 5·2*	Benzene 2·28*
[d]XII C_8H_{14} 	393·9° (79·36)	.. ..	389·2° (69·47)	367·1° (69·80)	350·0° (68·63)	315·6° (57·73)
[d]XIII C_8H_{14} 	510·7 (77·47)	.. ..	519·4 (74·11)	545·0 (79·58)	493·5 (74·49)	437·0 (68·05)
[c]XIV C_8H_{14} 	454·4 (85·21)	439·9° (81·02)	442·3 (82·31)	405·8 (80·48)	384·8 (68·55)	352·6 (71·37)
[c]XV C_8H_{14} 	465·0 (79·56)	440·8 (80·13)	425·8 (78·77)	401·6 (74·15)	401·6 (74·15)	355·4 (66·65)
[c]XVI C_8H_{14} 	480·0 (86·78)	451·3 (81·83)	448·9 (83·08)	433·2 (81·21)	424·6 (78·57)	367·1 (70·71)

* Dielectric constant of the solvent.

† Calculated value from the dispersion formula.

[a] B. K. Singh and R. K. Tewari, *Proc. Indian Acad. Sci.*, 1945, 22 A, 20.

[b] B. K. Singh and A. B. Lal, *Ibid.*, 1940, 12A, 157.

[c] B. K. Singh and B. Bhaduri, *Ibid.*, 1937, 6A, 340.

[d] B. K. Singh and T. P. Barat, *J. Indian Chem. Soc.*, 1940, 17, 1.

[e] B. K. Singh, B. Bhaduri and T. Barat, *Ibid.*, 1931, 8, 345.

the rotatory power of 2:5-dichloroanilinomethylenecamphor (I) is lower than that of *o*- and *m*-chloroanilinomethylenecamphors (VIII, IX); the rotatory power of 3-nitro-4-chloroanilinomethylenecamphor (II) is lower than that of *m*-nitroanilinomethylenecamphor (XII); and the rotatory power of *o*-, *m*-, and *p*-chloroanilinomethylenecamphors (VIII, IX, X) is lower than that of anilinomethylenecamphor (XVI) in all the solvents. (2) CH_3 group also, on account of its negative polarity, has a lowering effect on the rotatory power of the parent compound as is evident from the following observations (Table I): the rotatory power of 2-nitro-*p*-toluidinomethylenecamphor (III) is lower than that of *m*-nitroanilinomethylenecamphor (XII); the rotatory power of 3-nitro-*p*-toluidinomethylenecamphor (VI) is lower than that of *o*-nitroanilinomethylenecamphor (XI); and the rotatory power of *m*-and

p-toluidinomethylenecamphors (XIV, XV) is lower than that of anilinomethylenecamphor (XVI) in all the solvents; the rotatory power of 4-chloro-*o*-toluidinomethylenecamphor (V) is lower than that of *m*-chloroanilinomethylenecamphor (IX) in five solvents but *higher* in pyridine. There are, however, some deviations from the abovementioned generalization: the rotatory power of 4-nitro-*o*-toluidinomethylenecamphor (IV) is lower than that of *m*-nitroanilinomethylenecamphor (XII) in three solvents but *higher* in pyridine, chloroform and benzene; the rotatory power of 5-nitro-*o*-toluidinomethylenecamphor (VII) is lower than that of *p*-nitroanilinomethylenecamphor (XIII) in methyl alcohol but *higher* in acetone, pyridine, chloroform and benzene. (3) On the other hand, the positive-polarity of NO_2 group should raise the rotatory power of the parent compound. This is supported by the following observations (Table I): the rotatory power of 3-nitro-*p*-toluidinomethylenecamphor (VI) is higher than that of *p*-toluidinomethylenecamphor (XV), and the rotatory power of *p*-nitroanilinomethylenecamphor (XIII) is higher than that of anilinomethylenecamphor (XVI) in all the solvents; the rotatory power of *o*-nitroanilinomethylenecamphor (XI) is higher than that of anilinomethylenecamphor (XVI) in all the solvents except pyridine in which it is lower. But in the following three cases the NO_2 group is found to have a lowering effect on the rotatory power: the rotatory power of 3-nitro-4-chloroanilinomethylenecamphor (II) is lower than that of *p*-chloroanilinomethylenecamphor (X); the rotatory power of 2-nitro-*p*-toluidinomethylenecamphor (III) is lower than that of *p*-toluidinomethylenecamphor (XV); and the rotatory power of *m*-nitroanilinomethylenecamphor (XII) is lower than that of anilinomethylenecamphor (XVI) in all the solvents.

The effect of polarity of the substituent group is, with minor deviations, thus traceable in optical activity.

The position of the substituent group has also an effect on the rotatory power and is brought out in the following cases: 3-nitro-*p*-toluidinomethylenecamphor (VI), in which the NO_2 group is in the *o*-position to the substituted amino-group, has a higher rotatory power, whereas 2-nitro-*p*-toluidinomethylenecamphor (III) in which it is in the *m*-position to the substituted amino-group, has a lower rotatory power than that of *p*-toluidinomethylenecamphor (XV). Similarly, the rotatory power of *o*-nitroanilinomethylenecamphor (XI) and *p*-nitroanilinomethylenecamphor (XIII) is higher (except in pyridine in the former case), whereas the rotatory power of *m*-nitroanilinomethylenecamphor (XII) is lower than that of anilinomethylenecamphor (XVI). The NO_2 group raises the rotatory power when it is in

the *o*- or *p*-position to the substituted amino-group, whereas it lowers it when it is in the *m*-position.

EFFECT OF THE NATURE OF THE SOLVENT ON THE ROTATORY POWER

The specific rotatory power of these compounds for Hg_{5461} in six solvents is given in Table I. The sequences of decreasing rotatory power are as follows:—2: 5-dichloroanilinomethylenecamphor (I): methyl alcohol > pyridine > chloroform > acetone > ethyl alcohol > benzene; 3-nitro-4-chloroanilinomethylenecamphor (II): methyl alcohol > ethyl alcohol > acetone > pyridine > chloroform > benzene; 2-nitro-*p*-toluidinomethylenecamphor (III): methyl alcohol > ethyl alcohol > acetone > pyridine > chloroform > benzene; 4-nitro-*o*-toluidinomethylenecamphor (IV): pyridine > acetone > chloroform > ethyl alcohol > methyl alcohol > benzene. The sequence of decreasing (or increasing) rotatory power runs in the cases of 3-nitro-4-chloroanilinomethylenecamphor (II) and 2-nitro-*p*-toluidinomethylenecamphor (III) strictly parallel with that of the dielectric constants of the solvents, namely, methyl alcohol (31·2) > ethyl alcohol (25·8) > acetone (21·5) > pyridine (12·4) > chloroform (5·2) > benzene (2·28). A similar but less marked parallelism can be traced in the case of the other two compounds also, namely, the rotatory power of 2: 5-dichloroanilinomethylenecamphor (I) is highest in methyl alcohol, which has the highest dielectric constant, and lowest in benzene, which has the lowest dielectric constant, and the rotatory power of 4-nitro-*o*-toluidinomethylenecamphor (IV) is lowest in benzene.

It would, however, seem more rational to compare the rotatory power of a substance with the dielectric constant of its solution, and not of the solvent in which its rotatory power is determined. We have used the values of the dielectric constants of the solvents as we have not at our disposal the values of the dielectric constants of the solutions.

The abovementioned sequences of rotatory power in the different solvents are derived from the rotatory power measurements for Hg_{5461} (Table I). The choice of this wave-length is purely arbitrary as different sequences are obtained for other wave-lengths. For example, in the case of 4-nitro-*o*-toluidinomethylenecamphor (IV) the sequence for Hg_{5461} is pyridine > acetone > chloroform > ethyl alcohol > methyl alcohol > benzene, whereas that for N_{5893} is pyridine > ethyl alcohol > acetone > methyl alcohol > chloroform > benzene. These effects of dispersion can, however, be eliminated when compounds are found to obey the simple dispersion equation of Drude, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$. The rotation-constant (K) of this one-term equation can

be used as a measure of the absolute rotatory power of the substance. It refers to a wave-length λ, where $\lambda^2 - \lambda_0^2 = 1$ square micron, and it is not very much greater than 10,000 Å.U. The longest observed wave-length in our measurements is L_{6708} and an extrapolation from it to about 10,000 Å.U. is easily permissible in view of the linear nature of the dispersion equations obtained from our measurements. We have, therefore, also given in brackets (Table I) the values of K, the rotation-constant, as a measure of the absolute rotatory power of the compounds.

It will be seen that the value of K (Table I) in the different solvents runs parallel with that of the dielectric constant of the solvent in the case of 3-nitro-4-chloroanilinemethylenecamphor (II) and 2-nitro-*p*-toluidinomethylenecamphor (III). In the case of the other two compounds (I, IV) there is less strict parallelism: the value of K for 2:5-dichloroanilinomethylenecamphor (I) is lower in ethyl alcohol and higher in pyridine, and for 4-nitro-*o*-toluidinemethylenecamphor (IV) it is lower in methyl and ethyl acohols than the sequence of the dielectric constants of the solvents warrants it. This further emphasizes that the value of the dielectric constant of the solution rather than that of the solvent should be compared with the absolute rotatory power of the solution.

The compounds listed above in Table II are optically active nitro-dyes. They vary in colour from yellow to orange in the solid state or in alcoholic solution. When their alcoholic solution is made alkaline, the colour deepens in the case of the *ortho*- and *para*-nitro compounds (VI and VII,

EFFECT OF THE POSITION OF THE NITRO-GROUP ON THE COLOUR OF THE DYES

TABLE II

Substances	Colour in the solid state	Colour in ethyl alcohol	Colour in ethyl alcohol in presence of KOH
3-Nitro-*p*-toluidinomethylenecamphor (VI, Table I)	Orange-red	Yellow-orange	Port-wine-red
5-Nitro-*o*-toluidinomethylenecamphor (VII, Table I)	Bright yellow	Yellow	Deep violet
3-Nitro-4-chloroanilinomethylenecamphor (II, Table I)	Bright yellow	Lemon-yellow	Port-wine-red
2-Nitro-*p*-toluidinomethylenecamphor (III, Table I)	Lemon-yellow	Lemon-yellow	Yellow-orange
4-Nitro-*o*-toluidinomethylenecamphor (IV, Table I)	Lemon-yellow	Lemon-yellow	Yellowish-light-brown

TABLE III. 2: 5-*Dichloroanilinomethylenecamphors*

Solvent	Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentratration in gm./100 c.c.	*d* 0·5000	*l* 0·5000	*d* 0·5000	*l* 0·5000	*d* 0·5000	*l* 0·5000	*d* 0·5000	*l* 0·5000	*d* 0·5000	*l* 0·5000	*d* 0·5000	*l* 0·5000
Calculated $[\alpha]_{\lambda_0}$	$\pm \frac{60\cdot17}{\lambda^2-0\cdot1319}$ 0·3631		$\pm \frac{57\cdot76}{\lambda^2-0\cdot1342}$ 0·3664		$\pm \frac{58\cdot11}{\lambda^2-0\cdot1338}$ 0·3658		$\pm \frac{59\cdot45}{\lambda^2-0\cdot1327}$ 0·3643		$\pm \frac{57\cdot76}{\lambda^2-0\cdot1355}$ 0·3681		$\pm \frac{56\cdot94}{\lambda^2-0\cdot1326}$ 0·3641	
Line λ	Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
	d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Hg_{4358} ..	+1038·0°	−1032·0°	+1031·0°	−1030·0°	+1030·0°	−1029·0°	+1033·0°	−1034·0°	+1056·0°	−1055·0°	+993·0°	−990·0°
Li_{4603} ..	755·0	753·0	742·0	747·0	746·0	746·0	752·0	750·0	755·0	756·0	717·0	718·0
Cd_{4678} ..	694·0	693·0	684·0	683·0	682·0	681·0	692·0	691·0	694·0	693·0	662·0	661·0
Cd_{4800} ..	612·0	610·0	603·0	601·0	602·0	600·0	609·0	607·0	610·0	608·0	582·0	584·0
Cd_{5086} ..	473·0	473·0	465·0	464·0	464·0	463·0	472·0	471·0	471·0	470·0	452·0	450·0
Ag_{5209} ..	430·0	431·0	422·0	420·0	423·0	421·0	431·0	430·0	426·0	424·0	412·0	411·0
Hg_{5461} ..	360·0	362·0	351·0	352·0	352·0	354·0	358·0	361·0	356·0	354·0	344·0	342·0
Hg_{5780} ..	296·0	297·0	288·0	288·0	289·0	290·0	294·0	296·0	290·0	291·0	281·0	281·0
Na_{5893} ..	278·0	280·0	270·0	272·0	271·0	273·0	276·0	276·0	272·0	274·0	264·0	267·0
Li_{6104} ..	249·0	248·0	241·0	244·0	244·0	245·0	246·0	247·0	245·0	246·0	236·0	237·0
Cd_{6439} ..	214·0	215·0	207·0	208·0	208·0	209·0	212·0	213·0	208·0	209·0	202·0	203·0
Li_{6708} ..	188·0	190·0	181·0	182·0	182·0	184·0	186·0	189·0	183·0	185·0	177·0	178·0
	No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

TABLE IV. *3-Nitro-4-chloroanilinomethylenecamphors*

Solvent		Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentration in gm./100 c.c.		0·1000	0·1000	0·1000	0·1000	0·1000	0·1000	0·1000	0·1000	0·1000	0·1000	0·0500	0·0500
Calculated $[\alpha]_{\lambda_0}$		$\pm \frac{65\cdot59}{\lambda^2-0\cdot1268}$ 0·3561		$\pm \frac{65\cdot32}{\lambda^2-0\cdot1203}$ 0·3468		$\pm \frac{64\cdot45}{\lambda^2-0\cdot1200}$ 0·3464		$\pm \frac{61\cdot69}{\lambda^2-0\cdot1222}$ 0·3496		$\pm \frac{57\cdot11}{\lambda^2-0\cdot1201}$ 0·3465		$\pm \frac{54\cdot14}{\lambda^2-0\cdot1169}$ 0·3419	
Line λ		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
		d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{4800}	..	..	..	..	..	..	..	..	..	..	..	+480·0°	−470·0°
Cd_{5086}	..	+500·0°	−495·0°	+470·0°	−475·0°	+465·0°	−465·0°	+455·0°	−450·0°	+415·0°	−415·0°	390·0	380·0
Ag_{5209}	..	455·0	455·0	435·0	430·0	425·0	425·0	415·0	410·0	380·0	380·0	350·0	350·0
Hg_{5461}	..	380·0	385·0	365·0	370·0	360·0	365·0	350·0	345·0	320·0	315·0	290·0	300·0
Hg_{5780}	..	315·0	320·0	310·0	305·0	305·0	300·0	290·0	295·0	265·0	270·0	250·0	250·0
Na_{5893}	..	300·0	295·0	290·0	285·0	285·0	280·0	275·0	275·0	250·0	250·0	240·0	230·0
Li_{6104}	..	265·0	265·0	260·0	260·0	255·0	250·0	245·0	250·0	225·0	225·0	210·0	220·0
Cd_{6439}	..	235·0	230·0	230·0	225·0	225·0	220·0	210·0	215·0	195·0	190·0	190·0	180·0
Li_{6708}	..	200·0	210·0	195·0	205·0	190·0	195·0	185·0	185·0	175·0	175·0	160·0	170·0
		No mutarotation		No mutarotation		Shows mutarotation; after 24 hrs. $[\alpha]^{35°\,C.}_{Hg5461}$ for $d=295\cdot0°$ and for $l=290\cdot0°$		No mutarotation		No mutarotation		No mutarotation	

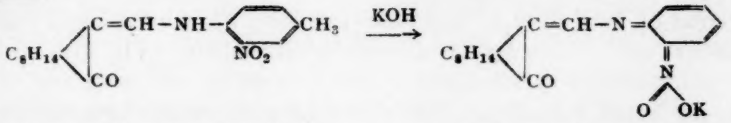
TABLE V. 2-*Nitro*-p-*toluidinomethylenecamphors*

Solvent		Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentration in gm./100 c.c.	*d*	0·2500		0·2500		0·2500		0·2500		0·2500		0·1000	
	l	0·2500		0·2500		0·2500		0·2500		0·2500		0·1000	
Calculated [α]		$\pm\frac{66\cdot68}{\lambda^2-0\cdot1271}$		$\pm\frac{66\cdot21}{\lambda^2-0\cdot1215}$		$\pm\frac{65\cdot54}{\lambda^2-0\cdot1206}$		$\pm\frac{65\cdot02}{\lambda^2-0\cdot1190}$		$\pm\frac{61\cdot26}{\lambda^2-0\cdot1127}$		$\pm\frac{52\cdot39}{\lambda^2-0\cdot1201}$	
λ_0		0·3565		0·3486		0·3472		0·3450		0·3357		0·3465	
Line λ		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
		d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{4800}	..	..	..	..	..	..	..	..	..	..	..	+475·0°	−470·0°
Cd_{5086}	..	+504·0°	−508·0°	+486·0°	−484·0°	+476·0°	−474·0°	..	..	+422·0°	−418·0°	375·0	375·0
$A\varsigma_{5209}$	..	464·0	464·0	440·0	442·0	436·0	436·0	+430·0°	−426·0°	390·0	388·0	345·0	350·0
Hg_{5461}	..	388·0	386·0	376·0	374·0	368·0	368·0	362·0	364·0	330·0	332·0	295·0	290·0
Hg_{5780}	..	324·0	322·0	314·0	312·0	308·0	306·0	304·0	302·0	278·0	276·0	245·0	245·0
Na_{5893}	..	302·0	302·0	292·0	290·0	290·0	288·0	288·0	286·0	264·0	264·0	230·0	235·0
Li_{6104}	..	268·0	270·0	266·0	262·0	258·0	260·0	254·0	254·0	2.8·0	238·0	205·0	210·0
Cd_{6439}	..	236·0	234·0	228·0	230·0	226·0	226·0	222·0	224·0	200·0	204·0	180·0	175·0
Li_{6708}	..	210·0	210·0	200·0	202·0	198·0	200·0	196·0	198·0	178·0	180·0	160·0	155·0
		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

TABLE VI. *4-Nitro-o-toluidinomethylenecamphors*

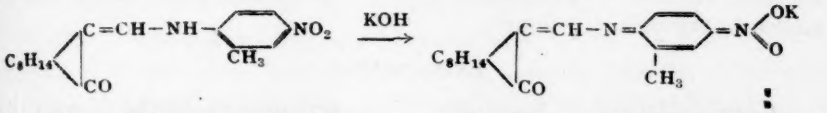
Solvent		Methyl alcohol		Ethyl alcohol		Acetone		Pyridine		Chloroform		Benzene	
Concentratration in gm./100 c.c.	*d*	0·5000		0·5000		0·5000		0·5000		0·5000		0·5000	
	l	0·5000		0·5000		0·5000		0·5000		0·5000		0·5000	
Calculated [α]		$\pm \frac{57\cdot16}{\lambda^2-0\cdot1342}$		$\pm \frac{57\cdot8}{\lambda^2-0\cdot1339}$		$\pm \frac{58\cdot58}{\lambda^2-0\cdot1329}$		$\pm \frac{58\cdot03}{\lambda^2-0\cdot1420}$		$\pm \frac{56\cdot38}{\lambda^2-0\cdot1381}$		$\pm \frac{55\cdot24}{\lambda^2-0\cdot1342}$	
λ_0		0·3664		0·3659		0·3645		0·3768		0·3716		0·3664	
Line λ		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
		d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*e*	*d*	*l*
Cd_{5086}	..	..	..	+461·0°	−464·0°	+461·0°	−464·0°	..	..	+471·0°	−467·0°	+445·0°	−443·0°
Ag_{5209}	..	+416·0°	−418·0°	420·0	419·0	421·0	423·0	+449·0°	−450·0°	422·0	424·0	404·0	4 2·0
Hg_{5461}	..	350·0	348·0	352·0	353·0	355·0	354·0	370·0	371·0	353·0	352·0	339·0	338·0
Hg_{5780}	..	285·0	284·0	289·0	288·0	293·0	292·0	302·0	303·0	287·0	287·0	276·0	276·0
Na_{5893}	..	269·0	270·0	273·0	272·0	272·0	273·0	231·0	284·0	268·0	270·0	260·0	258·0
Li_{6104}	..	240·0	240·0	242·0	243·0	245·0	247·0	253·0	250·0	241·0	239·0	233·0	231·0
Cd_{6439}	..	203·0	202·0	206·0	205·0	209·0	210·0	215·0	212 0	204·0	201·0	196·0	199·0
Li_{6708}	..	181·0	179·0	183·0	182·0	183·0	186·0	187·0	189·0	179·0	182·0	174·0	176·0
		No mutarota ion		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

Table II), whereas no such deepening of colour is observed in the case of the *meta*-nitro compounds (III and IV, Table II). This is due to the fact that *ortho*- and *para*-nitro derivatives can change in alkaline solution into the *aci*-form having quinonoid structure as illustrated in the following formulæ:



3-Nitro-*p*-toluidinomethylenecamphor (VI, Table II); yellow-orange in alcohol

2 conjugate double bonds (shortest route)
4 conjugate double bonds (longest route)
Port-wine red

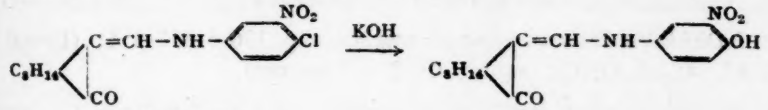


5-Nitro-*o*-toluidinomethylenecamphor (VII, Table II); yellow in alcohol

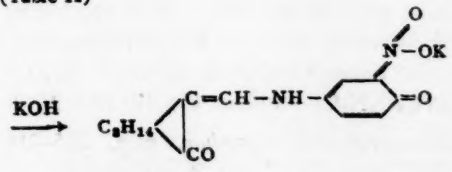
3 conjugate double bonds (either route)
Deep violet

Further, the chain of conjugate double bonds is longer in the *para*-quinonoid structure than that in the *ortho*-quinonoid structure; this explains the deeper colour of the *para*-nitro compound than that of the *ortho*-nitro compound.

The abovementioned tautomerisation to the *aci*-quinonoid form is not possible in the case of the *meta*-nitro compounds (III and IV, Table II); therefore, there is no change in colour when their alcoholic solution is made alkaline. The port-wine red colour of 3-nitro-4-chloroanilinomethylenecamphor (II, Table II), a *meta*-nitro derivative, in alkaline solution can, however, be explained by assuming that the Cl atom, which is rendered labile by the adjacent NO_2 group, is replaced by the hydroxyl group, thus permitting tautomerisation into the *ortho*-quinonoid structure:



II (Table II)



Our results are thus in agreement with the modern views of the influence of chemical constitution on colour.[4]

Dyeing Properties of Compounds II, III, IV and VI (Table II)

These substances, being acid dyes, have been examined for their dyeing properties on wool from an acid-bath containing 2% sulphuric acid and 10% Glauber's salt: 3-nitro-*p*-toluidinomethylenecamphor (VI) dyes wool a light yellow-orange colour which is fast to washing with soap and to sunlight (30 hours' exposure); 3-nitro-4-chloroanilinomethylenecamphor (II), 2-nitro-*p*-toluidinomethylenecamphor (III) and 4-nitro-*o*-toluidinomethylenecamphor (IV) dye wool light yellow colour which is fast to washing with soap. Sunlight, however, causes fading in these colours to a slight extent after a moderate exposure (12 hours).

Experimental

General Method of Preparation.—The *dextro*-forms of the compounds were prepared by adding oxymethylene-*d*-camphor (1 mol. proportion), dissolved in ethyl alcohol, to the solution of the free base in acetic acid, when a precipitate was obtained immediately or on keeping. It was then repeatedly recrystallised from ethyl alcohol.

The *lævo*- and *racemic*-isomers were prepared in the same way as the corresponding *dextro*-compounds and had similar crystalline form and solubility.

2: 5-*Dichloroanilinomethylene*-d-*camphor*, m.p. 139–140° C., was obtained as crystals with yellow tinge. It is very soluble in acetone, pyridine, chloroform and benzene, less so in methyl and ethyl alcohols, and insoluble in water. (Found: Cl, 21·89; N, 4·05. $C_{17}H_{19}ONCl_2$ requires Cl, 21·87; N, 4·32 per cent.)

2: 5-*Dichloroanilinomethylene*-l-*camphor*, m.p. 139–140° C. (Found: Cl, 21·92. $C_{17}H_{19}ONCl_2$ requires Cl, 21·87 per cent.)

2: 5-*Dichloroanilinomethylene*-dl-*camphor*, m.p. 136·5–137·5° C. (Found: Cl, 21·87. $C_{17}H_{19}ONCl_2$ requires Cl, 21·87 per cent.)

3-*Nitro*-4-*chloroanilinomethylene*-d-*camphor*, m.p. 215–216° C., was obtained as bright yellow rectangular plates. It is soluble in pyridine, less so in acetone, sparingly soluble in chloroform and methyl and ethyl alcohols, very sparingly soluble in benzene, and insoluble in water. (Found: Cl, 10·80; N, 8·19. $C_{17}H_{19}O_3N_2Cl$ requires Cl, 10·59; N, 8·37 per cent.)

3-*Nitro*-4-*chloroanilinomethylene*-l-*camphor*, m.p. 215–216° C. (Found: Cl, 10·77. $C_{17}H_{19}O_3N_2Cl$ requires Cl, 10·59 per cent.)

3-*Nitro*-4-*chloroanilinomethylene*-dl-*camphor*, m.p. 204–205° C. (Found: Cl, 10·79. $C_{17}H_{19}O_3N_2Cl$ requires Cl, 10·59 per cent.)

2-*Nitro*-p-*toluidinomethylene*-d-*camphor*, m.p. 193–194° C., was obtained as long lemon-yellow rectangular plates. It is soluble in pyridine, moderately soluble in acetone, chloroform and methyl and ethyl alcohols, sparingly soluble in benzene, and insoluble in water. (Found: N, 8·73. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

2-*Nitro*-p-*toluidinomethylene*-l-*camphor*, m.p. 193–194° C. (Found: N, 8·75. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

2-*Nitro*-p-*toluidinomethylene*-dl-*camphor*, m.p. 181–182° C. (Found: N, 8·72. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

4-*Nitro*-o-*toluidinomethylene*-d-*camphor*, m.p. 137·5–138·5° C., was obtained as lemon-yellow needles. It is very soluble in pyridine, chloroform, acetone and benzene, less so in methyl and ethyl alcohols, and insoluble in water. (Found: N, 8·71. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

4-*Nitro*-o-*toluidinomethylene*-l-*camphor*, m.p. 137·5–138·5° C. (Found: N, 8·73. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

4-*Nitro*-o-*toluidinomethylene*-dl-*camphor*, m.p. 139–140° C. (Found : N, 8·74. $C_{18}H_{22}O_3N_2$ requires N, 8·92 per cent.)

The rotatory power determinations were carried out in a 2-dcm. jacketed tube at 35° C. The value of λ_0, calculated from the dispersion formula, is given in the tables and is expressed as μ or 10^{-4} cm.

Summary

1. The rotatory dispersion of optically active forms of 2:5-dichloroanilino-, 3-nitro-4-chloroanilino-, 2-nitro-*p*-toluidino- and 4-nitro-*o*-toluidinomethylenecamphors has been investigated in six solvents for the visible spectrum (λ_{6708} to λ_{4358}), and found to obey the Drude's one-term equation, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$; it is therefore simple.

2. Within the limits of experimental error the *d*- and *l*-forms of these compounds possess identical rotatory power.

3. The effect of the polarities (as deduced from specific inductive capacity) of Cl, CH_3 and NO_2 groups on the rotatory power has been studied. With minor deviations, Cl and CH_3 groups, being negative, lower the rotatory power, whereas NO_2 group, being positive, raises the rotatory power. Thus the polar effect of substituent groups is traceable in optical activity.

4. Subject to minor deviations, the sequence (decreasing or increasing) of the rotatory power of these compounds runs parallel with that of the dielectric constants of the solvents in which the rotatory power is determined.

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